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COMPARATIVE ANALYSIS OF CONTAMINATED HEATING OILS

by

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Heating Fuels		Heating Oils		
Contamination		Hazardous Waste	14G	
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ABSTRACT

An exploratory investigation of the possible contamination of virgin heating oils by hazardous waste in the New Jersey/New York area was conducted. Twenty samples, including some that were suspected to be contaminated, were analyzed for 39 volatile organic compounds. In addition, total chlorine and water extractable chlorides were measured in 13 samples. A statistically valid sampling program to determine the extent of heating oil contamination in New York City was developed.

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SECTION 1

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

SUMMARY

This report summarizes an investigation of the potential contamination of virgin heating oil by hazardous waste. Residual oil (No. 5 and No. 6) and No. 4 oil are more likely to be contaminated than light distillate oils (No. 1 and No. 2). The heavier oils will tend to mask contaminants and the contaminants may not create any gross deterioration of burner performance.

New York and New Jersey account for 42.8 percent of United States deliveries of residual and No. 4 heating oil to the commercial sector (apartments, offices, general retail, etc.). A large fraction of this oil is used in the winter heating season. In addition, the northeastern New Jersey and New York metropolitan areas are very densely populated. The presence of major hazardous waste generators in the area and consideration of the above factors indicate the potential for more severe problems in the New Jersey/New York area than most other geographical areas.

A sampling strategy was developed to determine, in a statistically valid manner, the extent of heating oil contamination in New York City. Because it was suspected that only a few percent of the heating oil may be contaminated and there were more than 30,000 sites (heating units or storage tanks), a large number of samples would have been required. Specifically, if the true fraction of contaminated oil was 1 percent, there were 32,400 sites, and we were willing to accept a relative error of ±30 percent (a result of 1 ±0.3 percent), then 5,774 random samples would have been required. The large number of samples required for a statistically valid sampling program precluded its implementation.

Therefore, program objectives were redefined to conduct an exploratory analytical program using samples that had been previously collected by the states of New Jersey and New York and the city of New York. One of the primary objectives of the final program was to analyze a collection of virgin oil samples for 39 selected volatile organic compounds. No concentration data for these volatile organic compounds in virgin oils were available. A second, equally important, objective was to investigate chlorine speciation (organic vs. inorganic forms) in selected virgin oil samples. Unexpectedly high levels of chlorine had been previously found in some samples but no data were available to indicate whether the high chlorine levels were caused by salts (possibly from salt water) or contamination by chlorinated organic compounds. In addition, analyses of the samples for total bromine and fluorine were planned. The analytical methods to be employed in this program were described in a February 18, 1983 Quality Assurance Plan developed by GCA and approved by EPA.

Twenty samples (13 virgin oils and 7 waste oils) were selected for analysis of volatile organic compounds. Selection of the samples was based on the type of oil (No. 2, No. 4, No. 6 or waste), the source (terminal, refinery, apartment house, industry), the state or city where the sample was collected (New York, New Jersey, New York City), and preliminary indications of contamination or noncontamination.

Any general conclusions drawn from the exploratory analyses of such a limited collection of samples should only be made with extreme caution. In addition, some loss of volatile organic compounds may have occurred between the time that the samples were collected by the states in the fall of 1982 and the analysis by GCA in the spring of 1983. During this interim time period the samples were opened and analyzed under a separate program conducted by EPA Region II. When received at GCA, the sample containers were typically less than 50 percent full.

In this study, the word "contamination" is used to mean that the sample was found to contain at least one compound at a relatively high concentration compared to other oils of the same type. It does not imply any harmful environmental effect which must depend on toxicity, the effects of combustion, the extent of exposure, etc. Similiarly, statements that an oil is not contaminated imply that it is similiar to other oils of the same type but not necessarily that the normal components of an uncontaminated oil are not harmful. The ultimate impact of the volatile compounds found in contaminated and uncontaminated oil was not intended to be assessed in this study.

Selected examples of volatile organic compounds that were detected in the 13 virgin oil samples are presented in Table 1. Samples E, F, and N clearly appear to be contaminated. These three samples contain chlorinated organic compounds that are not found in other samples while sample E also contains relatively high concentrations of benzene, ethylbenzene, toluene and xylene. Note that samples E, F, and N were supplied as samples that were suspected to be contaminated. Sample K shows some slight evidence of contamination as it contains detectable concentrations of methylene chloride and 1,1,1-trichloroethane. Although Sample B appears to contain unusually high levels of ethylbenzene, toluene, and xylene, the data base which consists of only two samples of No. 2 oil is too small to develop any firm conclusions.

Selected examples of volatile organic compounds detected in the waste oil samples are presented in Table 2. These waste oil samples included automotive and industrial wastes that are apparently used as fuels. Some of the samples contain percentage levels of chlorinated organic compounds.

TABLE 1. SELECTED EXAMPLES OF COMPOUNDS DETECTED IN VIRGIN OIL SAMPLES, mg/kg[a]

	Sample Identification	A	B	C	D	E	F	G	H	I	J	K	L	M	N
	GCA Control No.	29639	29657	29646	29659	29661	29663	29641	29642	29643	29649	29660	29652	29656	29679
	State or City Sample Code	10683	20328	16379	22621	CE 156A	CE 158A	10692	12010	16375	19028	22623	19190	20327	A[b]
	Oil Grade	2	2	4	4	4	4	6	6	6	6	6	6	6	4
Compound	Oil Source	terminal	refinery	terminal	terminal	terminal	terminal	terminal	terminal	terminal	terminal	terminal	refinery	refinery	apartment
Benzene		< 20	110	46	45	590	140	23	< 2	15	30	37	28	15	<100
Ethylbenzene		240	970	160	120	2,500	240	94	< 2	47	30	230	110	21	580
Toluene		440	910	230	110	7,900	490	87	< 2	49	40	330	110	100	730
Xylene (isomers)		590	4,100	110	79	7,900	160	67	22	47	36	180	50	20	1,900
Methylene chloride		< 20	< 2	< 1	< 1	10	180	<1	< 2	<0.9	<1	11	<1	<0.9	< 20
Tetrachloroethene		< 20	< 2	< 1	< 1	140	140	<1	< 2	<0.9	<5	<1	<1	< 0.9	< 20
1,1,1-trichloroethane		< 20	< 2	< 1	< 1	950	1,900	<1	< 2	<0.9	<1	8	<1	< 0.9	3,900
Trichloroethene		< 20	< 2	< 1	< 1	<40	26	<1	< 2	<0.9	<1	<1	<1	< 0.9	< 20

[a] All samples are from New Jersey except 29679 which is from New York City.

[b] Sample from New York. Original sample code is 9-121-12-10-82-4.

TABLE 2. SELECTED EXAMPLES OF COMPOUNDS DETECTED IN WASTE OIL SAMPLES, mg/kg[a]

	Sample Identification	O	P	Q	R	S	T
	GCA Control No.	29665	29666	29669	29670	29675	29676
	State or City Sample Code	Site 9	Site 10	Site 20	Fabric and leather	WH187A	WH188A
Compound	Oil Source	NY	NY	NY	NY	NJ	NJ
Benzene		55	<3	520	100	< 90	< 80
Ethylbenzene		190	50	7,000	3,900	630	800
Toluene		480	<3	60,000	81,000	1,300	1,800
Xylene		110	93	35,000	19,000	2,700	3,300
Methylene chloride		15	<3	730	3,000	< 20	<20
Methyl ethyl ketone		<700	<300	34,000	95,000	< 2,000	<2,000
Tetrachloroethene		39	3,500	940	21,000	490	310
1,1,1-trichloroethane		970	17	1,400	28,000	270	420
Trichloroethene		5.6	440	450	14,000	< 20	< 20
Trichlorofluoromethane		510	<3	< 40	< 20	< 20	< 20
Methyl isobutyl ketone		<700	<2,000	17,000	18,000	< 2,000	< 2,000

[a] These "waste oils" are not, in general, typical automotive waste oils. They have been called waste oil because they are apparently burned as fuels.

Thirteen of the 20 samples analyzed for volatile organics were analyzed for total bromine, fluorine, and chlorine, and investigated for chlorine speciation. Total bromine concentrations in all samples were below the detection limit of 600 mg/kg. With the exception of two waste oil samples which contained 96 and 182 mg/kg, fluorine concentrations were below the detection limit of 50 mg/kg.

The results of the halogen analyses are summarized in Table 3. Many of the virgin oil samples do contain inorganic chlorides (water extractable chlorides) but these do not appear to account for the total chlorine. The unaccounted for chlorine may be attributable to the precision of the analytical methods or some of these samples may contain inorganic chlorides that are not extractable, semivolatile chlorinated compounds or volatile chlorinated organics for which analyses were not performed.

CONCLUSIONS

A small group of virgin fuel oil and waste oil samples was analyzed for 39 selected volatile organic compounds, chlorine, bromine, and fluorine. There may have been significant loss of volatile organic compounds prior to analysis by GCA because the samples were opened, partially analyzed under another project, and not maintained at 4°C in a headspace free condition. Many of the samples were selected for analysis because they were suspected or known to be contaminated. The results provide examples of the types of compounds and indications of the concentrations that may be found in contaminated oil. Any generalizations about the extent of contamination or the concentrations of contaminants in virgin fuel oil or waste oil are not appropriate.

Thirteen virgin fuel oil samples were analyzed for 39 selected volatile organic compounds. Three samples from terminals (E, F, and K) and one from an apartment house (N) were contaminated with volatile organic compounds. Contaminants that were identified in one or more of these samples are acetone, benzene, chloroform, 1,1-dichloroethane, ethylbenzene, methylene chloride, methyl ethyl ketone, tetrachloroethene, toluene, 1,1,1-trichloroethane, trichloroethene, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and xylene. Concentrations were in the range of 10 to 10,000 mg/kg.

Seven waste oil samples were also analyzed for volatile organic compounds. These samples may have included automotive waste oils and industrial chemical wastes that are apparently burned as fuel in New York. All the waste oil samples were contaminated with volatile organic compounds. Seventeen compounds with concentrations in the 6 to 95,000 mg/kg range were identified in one or more samples.

Ten of the previously discussed virgin fuel oil samples were analyzed for total chlorine, bromine and fluorine. Bromine concentrations were below 600 mg/kg and fluorine concentrations were below 50 mg/kg in all samples. Two samples that were previously identified as being contaminated with volatile organic compounds contained 1,366 and 5,560 mg/kg total chlorine.

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TABLE 3. SUMMARY OF HALOGEN RESULTS, mg/kg[a]

Compound	Sample Identification GCA Control No. State or City Sample Code Oil Grade Oil Source	B 29657 20328 2 Refinery	C 29646 16379 4 Terminal	D 29659 22621 4 Terminal	E 29661 CE156A 4 Terminal	H 29642 12010 6 Terminal	I 29643 16375 6 Terminal	J 29649 19028 6 Terminal	L 29652 19190 6 Refinery	M 29656 20327 6 Refinery	N 29679 A[a] 4 Apartment	O 29665 Site 9 Waste ---	Q 29669 Site 20 Waste ---	T 29676 WH 188A Waste ---
TOTAL CHLORINE		72	99	81	1,360	768	149	81	86	74	5,560	2,760	13,400	1,300
Water extractable chloride		<8	44	20	187	936	101	44	27	44	140	580	1,620	72
Chlorine detected in volatiles		<2	<1	<1	915	<2	<4	<5	<1	<0.9	3,100	1,260	3,300	670
TOTAL FLUORINE		<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	96	182	<50
Fluorine detected in volatiles		<2	<1	<1	<40	<2	<0.9	<1	<1	<0.9	< 20	71	112	< 20

[a] Total bromine was below 600 mg/kg in all samples. Volatile brominated organic compounds were not detected.

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Seven samples not contaminated with volatile organic compounds contained 72 to 146 mg/kg total chlorine while one sample contained 768 mg/kg total chlorine. Extraction of these ten samples with water typically demonstrated that a significant fraction, but not all, of the total chlorine appeared to be present as inorganic chloride. The unaccounted for chlorine may reflect the precision of the analytical methods, semivolatile chlorinated organic compounds, unanalyzed volatile chlorinated organic compounds or inorganic chlorides that were not extracted from the oil.

Three of the previously discussed waste oil samples were also analyzed for halogens. Total bromine was below 600 mg/kg in all samples. Two samples contained fluorine; 96 and 182 mg/kg. Total chlorine concentrations were in the 1,300 to 13,000 mg/kg range. Extractable inorganic chloride represented 5 to 25 percent of the total chlorine in these samples.

RECOMMENDATIONS

Further investigation of contaminated heating oil is recommended. The statistically and technically limited data set developed in this study provides new and interesting data but does not allow substantive conclusions with respect to environmental/health effects. In order to consider possible environmental/health effects, more information on the extent of contamination, the identity of all contaminants, the destruction efficiencies and emission rates, atmospheric dispersion, population exposure and health effects is needed. Specific recommendations are presented below:

1. The procedures used in this study to differentiate between inorganic chloride- and organic chloride-containing compounds in virgin heating oil appear to be useful and should be subjected to further investigations and validation.

2. If the determination of bromine- and fluorine-containing compounds in heating oil is important, further work on method development and validation should be done.

3. The extent of virgin heating oil contamination, the identity of the contaminants and the level of contamination should be defined in a larger statistically valid* sampling and analysis program. Samples should be collected from storage tanks at the points of use.

4. The destruction of the identified organic compounds in small boilers should be determined by reviewing theoretical analyses and current EPA waste oil investigations or conducting additional tests. Emissions of trace metals should also be evaluated in a similar manner.

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*During the peer review of this report, suggestions for a Minimum Initial Sampling procedure were provided. This statistical approach is designed to be an initial step with the goal of verifying contamination and indicating the order of magnitude.[1]

5. Emission estimates derived from the results of recommendations 3 and 4 should be used with dispersion models and population data to predict human exposure.

6. The health effects of the predicted human exposures should be evaluated to determine whether or not an environmental problem exists and the severity of any problem.

SECTION 2

INTRODUCTION

Investigations by the news media have indicated that some heating oils may be contaminated with potentially hazardous waste. On December 17, 1981, the ABC television program 20/20 reported on an investigation of "...deadly chemical wastes,...illegally mixed into heating fuel...."[2]

The initial objective of this EPA sponsored research program was to determine the extent of heating oil contamination in a statistically valid manner. A background investigation was conducted and the results were presented in an interim report.[3] During the background investigation, data on the distribution of heating oil were compiled. In addition, qualitative and anecdotal information on heating oil contamination was collected by discussions with industry and government organizations.

As a result of these preliminary investigations, it was decided to focus the remaining effort on the New York area. Data on the distribution of oil storage tank sizes and the total numbers of apartments and commercial establishments were collected. A statistically valid sampling strategy was developed through data inputs from this study and statistical analyses by an EPA consultant.[4] The results of the statistical analyses showed that a very large number of samples would be required to determine the extent of heating oil contamination in the New York City area. Thus, the large number of samples that would be required precluded the determination of the extent of heating oil contamination within the scope of this study. The development of a sampling strategy is summarized in Section 4 of this report as a basis for possible future investigations.

One of the concerns regarding contaminated heating oil is the possible presence of chlorinated organic compounds. These compounds are often toxic, difficult to burn and may, if not efficiently burned, form toxic byproducts during combustion. Investigations by the state of New York, New Jersey and EPA Region II during the fall of 1982 showed unexpectedly high levels of total chlorine in samples of virgin fuel oil obtained from terminals and refineries. It was suspected that the chlorine was present as inorganic chloride possibly from sea water contamination and thus not an environmental concern. However, data to support the above hypothesis were not available. The objective of this study was, therefore, redefined to perform laboratory analyses that would provide a better indication of whether the chlorine in selected samples was present as inorganic or organic compounds. Thirteen samples including virgin and waste oils were selected for analysis.

A second complimentary approach was to analyze directly for selected volatile organic compounds that might be responsible for contamination. Twenty samples were analyzed for 39 volatile organic compounds.

The oil distribution and consumption data are discussed in Section 3. Section 4 summarizes the statistically valid sampling strategy that was developed during this program. An overview of the analytical strategy and the selection of samples is presented in Section 5 while a more detailed discussion of the analytical methods is presented in Section 6. Quality Assurance is discussed in Section 7. The results of the analytical program are discussed in Section 8.

SECTION 3

HEATING OIL DISTRIBUTION AND CONSUMPTION

Distillate and residual fuel oils are distributed throughout the United States by a network which includes bulk terminals, bulk stations, pipelines, barges, tankers, tank trucks, and railroad tank cars. The major distinction between bulk terminals and bulk stations is that bulk terminals receive fuel oil by pipeline, ship, or barge, while bulk stations usually receive fuel by tank truck or rail car. There are approximately 1,900 bulk terminals and 15,000 bulk stations nationwide. In general, bulk terminals are larger and have higher throughputs than bulk stations. Tank trucks and rail cars transport the fuel oil from the bulk terminals and bulk stations to the consumer. However, some large consumers, such as electric utilities, may buy their fuel directly from the refineries. Figure 1 shows the location of petroleum refineries and the major flows of product in the United States.

The heavier fuel oils (No. 4 and residual oil) were the primary focus of this investigation because discussions with oil dealer associations indicated that if wastes were mixed with oil, they were likely to be mixed with No. 4 or residual oil. The dark color of these heavy oils can visibly mask waste contamination. In addition, the burners used to burn these heavy oils can handle some contamination without obvious adverse effects. On the other hand, contamination of distillate oils can adversely affect the performance of residential oil burners, thus requiring costly service calls.[3]

Table 4 shows 1980 deliveries of residual (No. 5 and 6 oil) and No. 4 oil.[5] Commercial use includes space heating, water heating, and cooking at non-manufacturing establishments such as apartment buildings, motels, restaurants, wholesale and retail businesses, health and educational institutions, and government office buildings. Large deliveries of residual and No. 4 oil to New York, New Jersey, California and Massachusetts are attributable to the high population and/or the high demand for heating. Other states with high populations and demands for heating fuels, such as the upper Midwest, rely heavily on natural gas. No explanation for the large amount of oil delivered to Louisiana is available except to note that the delivered oil may not be used in Louisiana.

The types of fuels used for space heating, in 1970, are shown in Table 5.[6] The data confirm that the use of oil for heating purposes is concentrated in the Northeastern part of the United States. More than 50 percent of the dwelling units in New York, New Jersey, Massachusetts, Delaware and Connecticut are heated by oil. Many of the other states in Table 4 and those not listed rely primarily on gas heat.

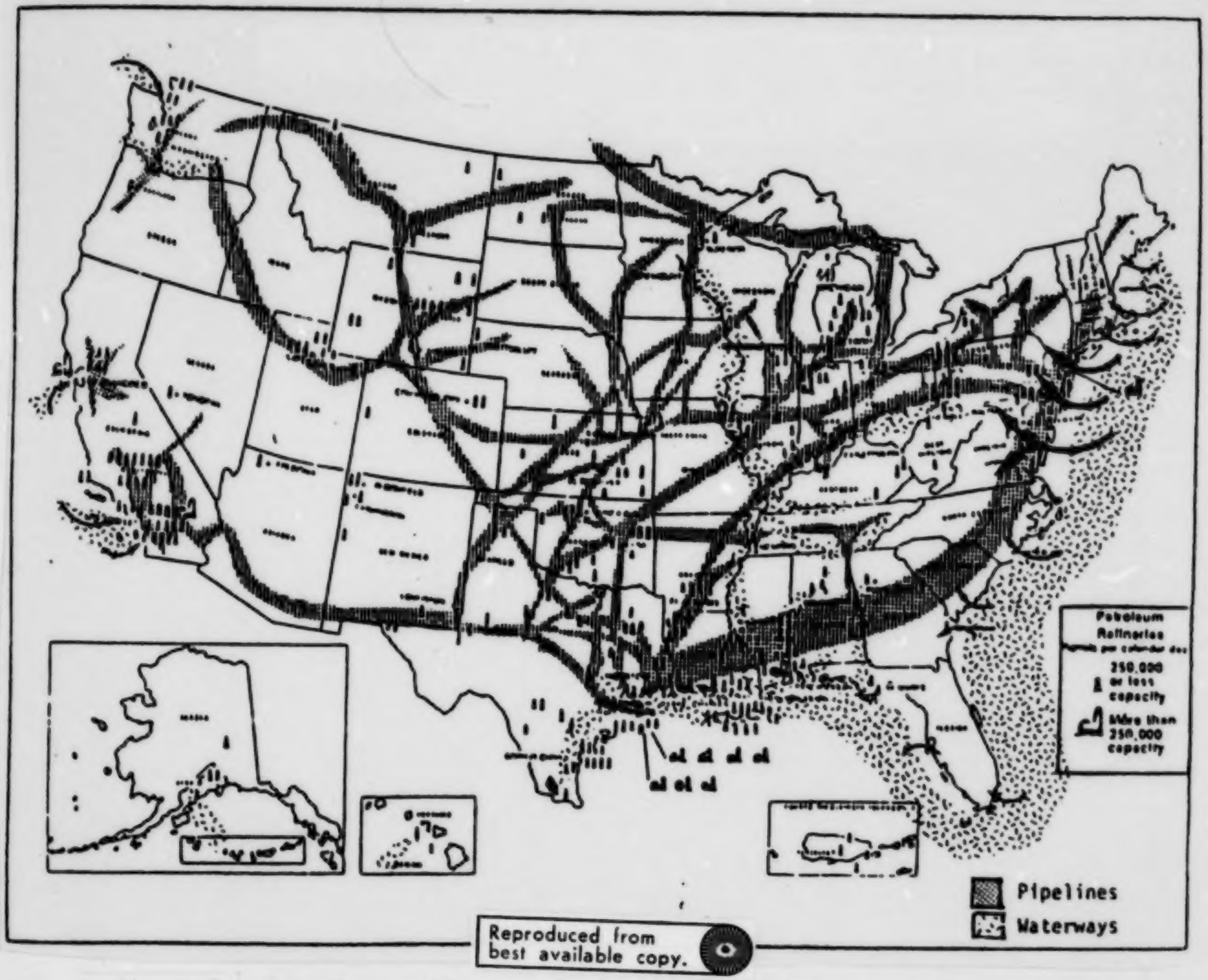
Petroleum
Refineries
barrels per calendar day
250,000 or less capacity
More than 250,000 capacity
Pipelines
Waterways

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Figure 1. Petroleum refineries and petroleum product transportation flows in the United States and Puerto Rico.

TABLE 4. RESIDUAL AND NO. 4 OIL DELIVERIES TO THE COMMERCIAL SECTOR[5]

	Residual deliveries		No. 4 deliveries		Residual and No. 4 deliveries	
	1,000 bbls	Percent of total	1,000 bbls	Percent of total	1,000 bbls	Percent of total
New York	25,482	28.3	6,007	45.9	31,489	30.5
Louisiana	13,493	15.0	1	0.0	13,494	13.0
New Jersey	10,972	12.2	1,738	13.3	12,710	12.3
California	6,825	7.6	113	0.9	6,938	6.7
Massachusetts	4,864	5.4	1,791	13.7	6,655	6.5
Delaware	4,274	4.7	41	0.3	4,315	4.2
Mississippi	3,412	3.8	0	0.0	3,412	3.3
Illinois	2,638	2.9	74	0.6	2,712	2.6
Texas	2,574	2.9	3	0.0	2,577	2.5
Indiana	2,436	2.7	72	0.6	2,508	2.4
Pennsylvania	1,524	1.7	420	3.2	1,944	1.9
Connecticut	1,173	1.3	1,068	8.2	2,241	2.2
38 Other States	10,638	11.2	1,759	13.4	12,397	12.0
U.S. TOTAL	90,005	100	13,087	100	103,092	100

TABLE 5. FUEL TYPE USED FOR SPACE HEATING, PERCENT OF HOUSING UNITS BY STATE[6]

	Natural gas	Fuel oil	Other
New York	38	57	5
Louisiana	82	0.5	18
New Jersey	41	53	6
California	86	0.7	13
Delaware	43	52	5
Massachusetts	28	66	6
Mississippi	70	22	8
Illinois	71	14	15
Texas	79	0.4	21
Indiana	57	27	16
Pennsylvania	48	35	17
Connecticut	21	72	7

New Jersey has a population of 7,400,000 and the highest state population density (986 people/square mile) in the United States.[7] New York City, with a population of 7,900,000, is the largest city in the United States and has a population density of 23,455 people/square mile.[7]

New York and New Jersey were selected as the principal areas of investigation for this program based on the facts discussed above and several other relevant factors. These states are heavily industrialized and have major hazardous waste generators. One study has indicated that, despite the small geographical area, industry in EPA Region II (New York, New Jersey and Puerto Rico) generates 15 percent of the U.S. hazardous waste total[8]. In addition, New Jersey contains 85 of the 546 Superfund sites. No other state contains more than 46 Superfund sites.[9] There was existing evidence that some heating oils in the New York/New Jersey area were contaminated. Federal, state and local government officials were actively investigating waste oil and heating oil contamination in these states.

SECTION 4

NEW YORK SAMPLING REQUIREMENTS

The development of a statistically valid plan for determining the extent of heating oil contamination in New York City was initially an important goal of this project. The plan was designed to determine the fraction of oil in storage tanks at apartments and other commercial facilities that is contaminated at any given time. In order to estimate the number of samples required to achieve a specific confidence interval for the fraction of contaminated oil, estimates for the following four variables were required:

- number of storage tanks, (N)
- coefficient of variation of the tank size, C(X)
- hypothetical fraction of contaminated oil, P
- maximum relative error, d

The formulae, developed by an EPA Consultant, Dr. James Dunn, to calculate the required sample size are presented in Table 6.[4] Meetings and telephone discussions were held with personnel from the New York State Department of Environmental Conservation, the New York City Department of Environmental Protection, Region II of the U.S Environmental Protection Agency and the New York City Fire Department in order to develop estimates for N, C(X) and P.

The number of storage tanks (N) was estimated to be 32,400 based on a meeting with Mr. Sam Lieblach of the New York State Department of Environmental Conservation.[10,11] He used data on the amount of fuel used in New York City, the typical heating unit size and the available inventory data to estimate that there are 32,400 oil fired heating units. We have assumed that there is one storage tank for each heating unit.

In order to determine the coefficient of variation of the storage tank sizes, actual data on a selected number of tanks were needed. Street addresses and facility data (size of apartment, etc.) were selected randomly from New York City Department of Environmental Protection files. The street addresses were submitted through EPA Region II to the New York City Fire Department. Fire Department personnel searched their files and reported the storage tank sizes for 78 sites. The data are shown in Table 7. The mean tank size was 6,013 gallons with a standard deviation of 4,896 gallons and a coefficient of variation, C(X), of 0.81.

TABLE 6. FORMULAE TO CALCULATE MINIMUM SAMPLE SIZES (n) FOR ESTIMATION OF THE OVERALL FRACTION OF CONTAMINATED FUEL[4]

---

(1) $n \geq n_o/(1 + n_o/N)$

where:

n = minimum sample size

n_o = see formula 2

N = number of storage tanks

(2) $n_o = Z^2 \ (1-P) \ [1 + C^2 \ (X)] \ d^2 \ P$

where:

Z = critical value from a normal distribution table

P = Fraction of oil that is contaminated

$C(X)$ = coefficient of variation or relative standard deviation, see formula 3

d = maximum relative error

(3) $$C(X) = \sqrt{\frac{\sum_{i=1}^{N} X_i^2 - 1/N \ {\sum_{i=1}^{N} X_i}^{2}}{N-1}} \Bigg/ \overline{X}$$

where:

X_i = size of individual storage tank

$\overline{X}$ = mean storage tank size. Note that $C(X)$ is estimated from the sizes of a selected group of storage tanks.

TABLE 7. NEW YORK CITY OIL STORAGE TANK SIZES, TYPE OF OIL AND FACILITY DATA FOR 78 RANDOM FACILITIES

Storage tank size,[a] gallons	Type of oil	Number of dwelling units
Manhattan[b]		
5,000	6	18
10,000	2	114
4,000	6	40
4,000	6	28
7,500	6	--
4,000	6	41
5,000	6	41
3,000	6	81
4,000	6	61
4,000	6	60
4,000	2	30
5,500	6	Hotel
3,000	5	School
5,000	6	202
4,000	4	32
2,000	4	45
7,000	6	Commercial
5,000	6	50
15,000	6	206
275	2	Hotel
3,500	4	28
3,000	6	Commercial
30,000	4	300
6,000	4	42
4,500	6	Commercial
9,000	6	164
5,000	6	47
10,000	6	26
1,000	6	167
4,000	4	Commercial
Bronx[c]		
15,000	6	120
5,000	2	50
3,000	4	24
5,000	4	16
5,000	6	64
5,000	6	60
5,000	6	56
5,000	6	86
3,300	4	40
5,000	6	62
5,000	4	5
3,000	4	Commercial
Queens[d]		
15,000		144
5,000		56
5,000		59
2,000		292

(continued)

TABLE 7 (continued)

Storage tank size,[a] gallons	Type of oil	Number of dwelling units
Queens (continued)		
20,000		136
6,000		180
10,000		Nursing home
3,000		32
4,000	2	60
5,000	4	54
10,000	6	Commercial
4,000	4	46
3,000	6	61
3,000	6	61
2,500	6	48
3,000	6	32
16,000	6	168
3,000	2	Commercial
5,000	6	130
Brooklyn[e]		
4,000	6	16
5,000	6	72
1,500	6	102
5,000	6	124
4,000	4	60
4,000	4	30
3,000	6	72
3,000	6	44
2,750	4	33
2,500	4	33
2,500	4	36
2,250	4	33
Staten Island[f]		
15,000	6	162
15,000	6	149
15,000	6	---
10,000	4	150

[a] The mean tank size for the 78 sites was 6,013 gallons. The standard deviation was 4,896 gallons and coefficient of variation was 0.814.

[b] Mean = 6,209 gallons, standard deviation = 5,374 gallons, coefficient of variation = 0.866.

[c] Mean = 4,944 gallons, standard deviation = 3,345 gallons, coefficient of variation = 0.677.

[d] Mean = 6,552 gallons, standard deviation = 5,709 gallons, coefficient of variation = 0.795.

[e] Mean = 3,250 gallons, standard deviation = 1,133 gallons, coefficient of variation = 0.349.

[f] Mean = 13,750 gallons, standard deviation = 2,500 gallons, coefficient of variation = 0.182.

It is not practical to select a single value for the hypothetical fraction of contamination, P, or the maximum relative error. Based on discussions and meetings with involved local environmental officials during the late fall of 1982, we established a 1 percent (P = 0.01) contamination level as a reasonable guess for planning purposes. The acceptable maximum relative error (d) requires a judgment with regard to the tradeoff between the error and the required sample size. Required sample sizes for contamination fractions between 0.00333 and 0.12 and for maximum relative errors between 0.1 and 0.4 are presented in Table 8. The data in Table 8 show that if we assume a hypothetical contaminated oil fraction of 0.01 and we are willing to accept a maximum relative error of 0.3, then we should plan to obtain 5774 samples. If the measured fraction of contamination in 5774 samples proved to be 0.01, then we would be 95 percent confident that the true fraction of contamination was 0.01 ± 0.003. Review of the data in Table 8, showed that too many samples would have been required to implement this sampling and analysis program within the scope of this project.

TABLE 8. MINIMUM SAMPLE SIZES (n) FOR ESTIMATION OF THE OVERALL FRACTION OF CONTAMINATED FUEL[a]

$$n \geq n_o/(1 + n_o/N)$$

where $n_o = z^2(1 - P)[1 + C^2(X)]/d^2P$,

$z = 1.96$,

$C(X) = 0.81415$ = coefficient of variation,

$N = 32400$ = number of storage tanks

P = fraction of oil that is contaminated,

d = maximum relative error

	Maximum Relative Error (d)			
P	0.1	0.2	0.3	0.4
0.00333	27701[c]	19303	12823	8723
0.01	21424	10625	5774[d]	3523
0.03	12614	4454	2143	1241
0.06	7646	2323	1075	614
0.09	5385	1538	702	399
0.12	4093	1130	512	290

[a] Based on Reference 4. See formulae in Table 6.

[b] P = fraction of oil that is contaminated.

[c] Minimum sample size (n).

[d] An example of the application of this table follows. If the best estimate for the fraction of oil that is contaminated is 0.01 (1 percent) and one wants to limit the maximum relative error to 0.3 (be 95 percent confident that the percentage of contaminated oil is 1 ± 0.3 percent) then one should plan to collect 5774 samples.

SECTION 5

SAMPLING AND ANALYSIS PROGRAM

BACKGROUND

The results of the statistical analyses, discussed in Section 4 and presented in more detail in Reference 4, were presented in a meeting at the U.S. Environmental Protection Agency's Region II office on December 3, 1982.[12] Representatives from EPA-Region II, EPA-IERL/RTP, New York City Department of Environmental Protection, New York State Department of Environmental Conservation, New Jersey Department of Environmental Protection, and GCA attended the meeting. Opinions regarding the need to define the extent of heating oil contamination varied. Some attendees felt that defining the extent of heating oil contamination was of primary importance although some state representatives had concluded the existence of a problem and were proceeding to develop regulations. All parties agreed that resources to implement a statistically valid sampling program were not available and that redefinition of program objectives was needed.

Accordingly, the discussion centered around possible chemical analyses that might be conducted by GCA under this project. Several options were discussed but again opinions on the utility of the chemical analyses were quite varied. The high (hundreds of ppm) levels of total chlorine detected in some virgin oil samples previously analyzed by Engineering Science were of some concern to everyone. There was speculation that the high total chlorine levels were caused by contamination from salt water and thus were largely inorganic chlorides. However, it was not clear that any data existed to support this contention. It was agreed that there was a need to define an analytical method to determine the inorganic chloride content of the oil samples and to develop some data on the levels of inorganic chloride. The possibility of extracting inorganic chlorides by mixing the oil samples with water was discussed.

Several other options for chemical analyses to evaluate volatile chlorinated organic compounds, volatile organic compounds, semivolatile compounds and trace metals were discussed. However, there was no consensus at the meeting with regard to the utility of these analyses.

Subsequent to the meeting, GCA prepared two analytical options for consideration by the EPA-IERL/RTP project officer.[13] The first option consisted of the following:

- Analyze each oil sample for selected volatile organic compounds by purge and trap GC/MS procedures.
- Analyze each oil sample for total chlorine, bromine and fluorine. Prepare samples by Parr bomb combustion and use ion chromatrography for quantitation.
- Mix each oil sample with water. Separate the phases. Analyze each phase for Cl, Br, and F. Analyze the water phase for total organic halogens.

The second option consisted of the following:

- Analyze a larger group of samples for volatile organic compounds by purge and trap GC/MS procedures.

The volatile organic analyses were suggested because they might demonstrate that the chlorine in the oil was not totally inorganic chloride and the data might provide some examples of contamination by specific chlorinated organic compounds. The primary objective of the aqueous extraction was to provide some indication of whether the chlorine in the oil was present in inorganic or organic compounds. It was hoped that the total organic halogen analysis of the water phase would confirm that the water was extracting only inorganic halogens. The Br and F analyses were included because it was anticipated that these elements would be easily measured and would provide new data. In general the intent of these limited analyses of a small number of possibly contaminated samples was to provide some interesting data that might be expanded upon in future more comprehensive programs.

During subsequent discussions with the EPA-IERL/RTP project officer, it was decided to implement a program consisting of both options; some samples would be analyzed according to the option one approach while some samples would be analyzed only for volatile organic compounds.

SAMPLE COLLECTION

As a result of the December 3, 1982 meeting discussed above, it was decided that GCA would not participate in any fuel oil sampling activity. Rather, it was decided that the planned analyses would focus, primarily, on suspected contaminated samples that had been previously collected by New York and New Jersey in the fall of 1982. In general these samples were collected in accordance with procedures suggested by Engineering-Science[14] and subsequently described in a recent technical paper.[15] Whenever possible, precautions were used to obtain representative samples by taking aliquots from different levels in the tank. Engineering Science procedures called for preparation of a 750 ml composite sample by transferring equal portions from each of three levels to a clean glass bottle with enough head space to allow for expansion. The samples were delivered by New York and New Jersey to Engineering Science's McLean, Virginia office. From there, they were transported, by air, to Engineering Science's laboratory in California where analyses were conducted for Cl, Br, PCB, total volatiles, sulfur, ash, heating value and ten trace elements. The samples were then sent back to New York and New Jersey.

SAMPLE SELECTION

In order to expedite the analytical program, GCA requested, in a January 18, 1983 letter, assistance from EPA Region II to obtain a comprehensive group of 30 specific samples.[16] The objective was to proceed with the process of obtaining the samples while final sample selection proceeded. A few days later suggestions were received from EPA statistical consultant (Dr. James Dunn) and the list was expanded by a telephone call to EPA Region II. A total of 44 samples were requested from Region II in order to include all possible samples that might be of some interest. EPA Region II arranged for delivery of the samples, from New York and New Jersey, to their New York City office. GCA personnel picked the samples up in New York and returned them by car to Bedford, Mass. The samples were logged in and stored in GCA's room temperature sample bank on January 31, 1983.

The list of available samples and preliminary selection of a subset of these samples for analyses was briefly reviewed with the Project Officer on February 8, 1983 at IERL-RTP. Final sample selection was made by GCA in late February when review of available funds indicated that we could analyze 13 samples by the option 1 scheme and 7 samples by the option 2 scheme if the analysis of the oil phase was deleted from option 1.

The factors that were considered in the final sample selection process are listed below:

- Preliminary data on total chlorine concentration,
- Type of oil (#2, #4, #6, waste oil),
- Dr. James Dunn's suggestions,
- Source of oil (refinery, terminal, industry, apartment house),
- Number of samples of the same type and source,
- State or City of origin (New Jersey, New York or New York City),

Headspace was not considered in the selection of samples because all the samples contained headspace.

Dr. James Dunn's statistical selection of samples was designed to identify the best species to differentiate contaminated and uncontaminated fuels. He selected five virgin oils that appeared to be contaminated, five that appeared to be uncontaminated, and five waste oils from New Jersey. Four of the five contaminated oils selected by Dr. Dunn were included in the final group. One of his alternate selections was substituted for the fifth contaminated oil. Only one of his suggested clean oil samples was selected because we wanted to focus more heavily on contaminated oils. Only one of his waste oil samples was selected because the oils were from New Jersey, it was desired to allocate a reasonable number of analyses to New York state samples which were all waste oils and we did not want to overemphasize waste oils.

The selection of samples for analysis is summarized in Table 9. In general, preference was given to the heavier (No. 4 and No. 6) virgin fuel oils that were the most likely candidates for contamination. A few waste oils were analyzed because they are a potential contaminant and because one of the objectives was to analyze some New York State samples which only consisted of waste oil. A small number of No. 2 oil samples was analyzed to complete the data base. A second important selection criteria was the preliminary data from Engineering Science on the total chlorine concentrations. Generally, samples with high total chlorine concentrations were selected.

In summary, a total of 44 samples were delivered to GCA laboratories for possible analysis. From this population, only volatile organic analysis were conducted on 7 samples, while halogen and volatile organic analyses were performed on an additional 13. The distribution of analyses as a function of oil sample type can be determined from Table 9.

FINAL ANALYTICAL PROGRAM

One objective of the final analytical program was to provide some indication as to whether the chlorine in some example samples was present as inorganic or organic compounds. It was anticipated that the ion chromatography procedure, utilized to quantitate chloride, would also serve to provide data on bromide and fluoride. A second objective was to analyze for selected volatile organic compounds. For the most part, this was viewed as an exploratory analytical program. The intent was to provide some new data on a very limited and, admittedly, nonrepresentative group of oils. It was agreed that if the chlorine speciation analysis proved to be successful, then a more comprehensive program might be pursued by EPA in the future.

High total chlorine levels in virgin oils were first noted in the fall of 1982. However, no information on whether the chlorine was present as inorganic or organic compounds was available at that time. In addition there was no established analytical method to differentiate between organic and inorganic forms of chlorine. As part of this program a water extraction procedure was proposed to remove inorganic chlorides from the oil. In addition, it was proposed to check the aqueous phase for total organic halogens to make sure that organic chlorinated compounds were not being extracted by the water.

When this program was initiated, no data on the types or concentrations of volatile organic compounds suspected to be found in virgin oils were available. It was our intent, therefore, to analyze a small group of samples to develop some new data and possibly find some examples of the types of volatile organic compounds that can be present in contaminated oils. The

TABLE 9. SUMMARY OF SAMPLE SELECTION METHODOLOGY

Sample type	Number available	Number Analyzed		Reasons for selection
		Volatile organic compounds	Halogens	
No. 2	6	2	1	Contamination not suspected. Minimum number of samples were selected. One terminal sample was selected for volatile analysis. One refinery sample was selected for volatile and halogen analyses.
No. 4, partially analyzed	4	2	2	The two samples that appeared to have the highest total chlorine concentrations were selected.
No. 4, not partially analyzed but contamination suspected	4	2	1	Results were potentially interesting to New Jersey. First samples on list were selected.
No. 6, Refineries	5	2	2	Two samples with apparent high total chlorine concentrations that were selected by Dr. James Dunn were analyzed.
No. 6, Terminals	7	5	3	An important group of samples with apparent high total chlorine concentrations. Samples selected by Dr. James Dunn and other samples with high total chlorine concentrations were analyzed.
Waste Oil, New Jersey	7	2	1	Waste oil was not an important category. No special selection criteria were used.
Waste Oil, New York	7	4	2	EPA-IERL/RTP wanted to analyze some New York samples. Samples with strong evidence of contamination were selected.
No. 4 and No. 6, New York City	4	1	1	A sample that was known to be contaminated and was collected from an apartment house was analyzed.
Total	44	20	13	

emphasis was placed, therefore, on oil samples that were suspected to be contaminated, although other samples were analyzed in order to develop some baseline data. Again it was expected that the results might be interesting but would not provide definitive answers on the extent of contamination, the concentrations or the type of contaminants. Such answers could only be provided through a larger sampling and analysis program. However, because no data on the volatile organic compounds and halogen species addressed in this analytical program were available the results would necessarily lead to some expansion of the data base consistent with available funding. The analyses planned for the final analytical program are shown in Figure 2.

On February 18, 1983 a revised Quality Assurance Project Plan was submitted to EPA[17] incorporating several modifications to the original September 1982 Quality Assurance Project Plan[18] brought about by changes in overall program objectives. Analyses for physical characteristics, semivolatile organics and trace elements were deleted from the original QA Plan. Information on the analyses for chlorine, bromine, fluorine and the water extraction procedure were added to the QA Plan.

The original September 1982 QA plan was found by EPA to be conditionally acceptable because the statistical method to select sample sites was not included. As previously discussed, the selection of a statistically representative sample population proved to be beyond the scope of the study as too many samples were required. Therefore, the plan was revised to delete the statistical selection of samples and to include only the analysis of heating oil and waste oil samples that had been previously collected by the New York Department of Environmental Conservation, the New York City Department of Environmental Protection, and the New Jersey Department of Environmental Protection. Because GCA was not to collect the samples, the description of the sampling procedures was revised. The original QA Plan stated that GCA would collect the samples in duplicate VOA vials, store the vials in ice and ship them to the laboratory within 24 hours. The revised plan stated that the sample collection and preservation procedures would vary depending on which organization handled the samples and that aliquots of some samples collected in 1 quart jars had been partially analyzed. The revised QA plan was approved by EPA on February 24, 1983.[18] Laboratory analyses were started in March 1983.

Analysis of the oil phase (see Figure 2) although originally planned, was not included in the revised QA plan and not conducted. The analysis of the oil phase was originally included in order to track the chlorine through the analytical system. However, further consideration of the possible results showed that they would probably not be very significant and would not justify the required reduction in the already limited number of samples. If there were no volatile chlorinated organics in the sample or if no volatile chlorinated organics were lost in the extraction process, it would have been possible to calculate a mass balance for Cl. However, the validity and usefulness of this calculation is questionable as discussed in Appendix A, wherein four possible hypothetical situations are investigated.

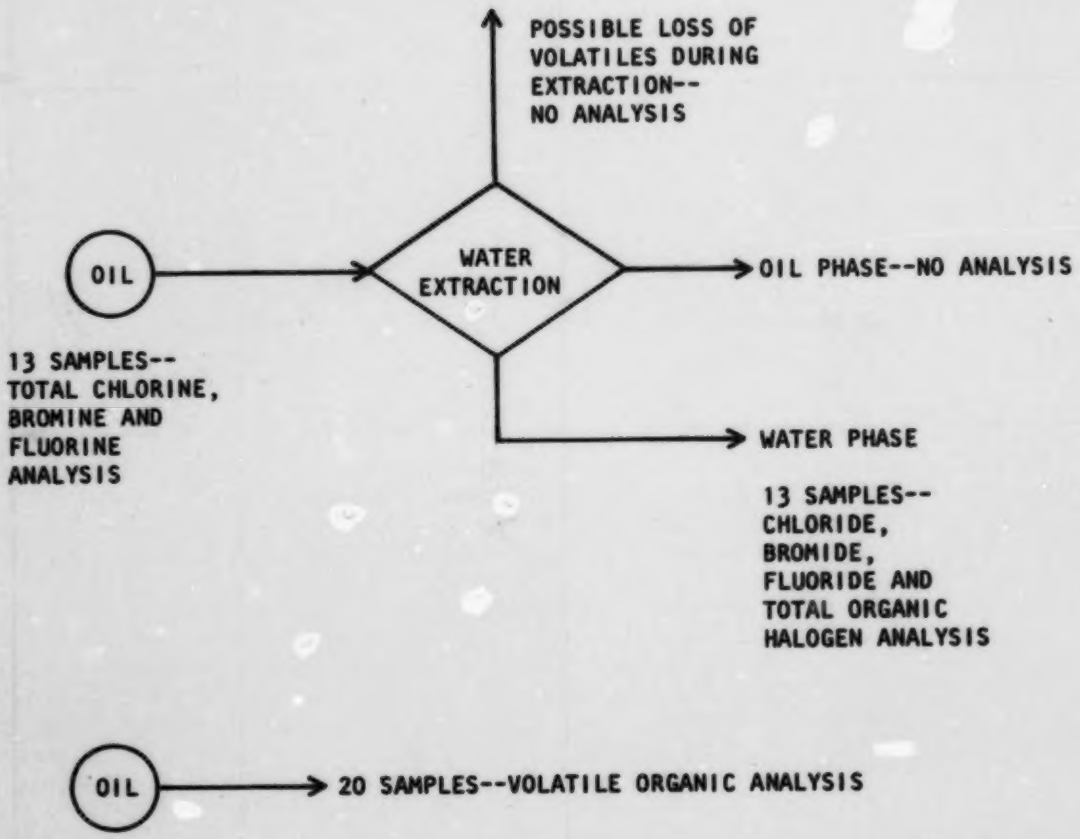
POSSIBLE LOSS OF VOLATILES DURING EXTRACTION--NO ANALYSIS
OIL
WATER EXTRACTION
OIL PHASE--NO ANALYSIS
13 SAMPLES--TOTAL CHLORINE, BROMINE AND FLUORINE ANALYSIS
WATER PHASE
13 SAMPLES--CHLORIDE, BROMIDE, FLUORIDE AND TOTAL ORGANIC HALOGEN ANALYSIS
OIL
20 SAMPLES--VOLATILE ORGANIC ANALYSIS

Figure 2. Planned analyses of oil samples.

SECTION 6

LABORATORY PROCEDURES

SAMPLE RECEIPT AND CHAIN OF CUSTODY

On January 31, 1983, a set of 44 oil samples was delivered to the GCA/Technology Division Sample Bank in Bedford, Massachusetts. All samples were accompanied by chain of custody documentation; these records were signed by Sample Bank receiving personnel and entered in the permanent project file.

Routine inspection upon receipt revealed all samples to be clearly identified and in good condition; there were no discrepancies between the sample labels and submitted sample custody records, and no breakage or leakage was noted. Samples were received at ambient temperature in the following types of containers:

• 32 samples:	1-liter narrow-mouth clear glass bottles with plastic screw caps,
• 7 samples:	40-ml clear glass vials with septum-seal screw caps,
• 4 samples:	500-ml wide-mouth clear glass jars with metal screw caps, and
• 1 sample:	500-ml narrow-mouth amber glass bottle with plastic screw cap.

Upon receipt, the submitted samples were entered in the Master Log Book and assigned individual GCA Control Numbers. This unique identification was affixed to the respective sample containers and subsequently used throughout the laboratory procedures for positive traceability. A cross-reference list of the samples received and their corresponding GCA Control Numbers is shown in Table 10.

Chain of custody procedures were maintained in the laboratory through the use of GCA Custody Notebooks. At the time of receipt, a page for each sample was entered sequentially by GCA Control Number in the Custody Notebook, and the samples were transferred to the locked Sample Bank for storage until the time of analysis. Subsequent handling of the samples was documented by signed entries in the Custody Notebook. In addition, the transfer of samples between analysts within the laboratory was documented on Sample Custody Transfer forms which become part of the permanent project file and serve as a supplement to the Custody Notebook record of sample handling.

TABLE 10. CROSS-REFERENCE LIST OF SAMPLES RECEIVED

Type of container		Sample identification	GCA Control No.
1-liter narrow-mouth clear glass bottle	Sample Volume from 200 ml to 300 ml	10683	29639
		10684	29640
		10692	29641
		12010	29642
		16375	29643
		16377	29644
		16378	29645
		16379	29646
		16381	29647
		16860	29648
		19028	29649
		19188	29650
		19189	29651
		19190	29652
		19191	29653
		19192	29654
		20326	29655
		20327	29656
		20328	29657
		22510	29658
		22621	29659
		22623	29660
		CE 156A	29661
		CE 157A	29662
		CE 158A	29663
500-ml narrow-mouth amber glass bottle	Sample Volume 250 ml	CE 159A	29664
40-ml clear glass vial	Sample Volume from 10 ml to 30 ml	ES-821203	29665
		ES-821204	29666
		ES-821205	29667
		ES-821207	29668
		ES-821208	29669
		ES-821219	29670
		ES-821221	29671
1-liter narrow-mouth clear glass bottle	Sample Volume from 200 ml to 300 ml	LM 2002A	29672
		WH 185A	29673
		WH 186A	29674
		WH 187A	29675
		WH 188A	29676
		WH 190A	29677
		WH 193A	29678
500-ml wide-mouth clear glass jar	Sample Volume from 100 ml to 400 ml	9-121-12-10-82-4	29679
		13-121-12-21-82-6	29680
		28-163-12-16-82-6	29681
		55-121-12-28-82-6	29682

TOTAL HALOGEN ANALYSIS

Introduction

Review of current methodologies applicable to the analysis of total halogens in oils contributed the following:

- ASTM D 808-63 (Reference 20)
- ASTM D 1317-64 (Reference 21)
- XRF (Reference 22)
- NAA (Reference 23)

Criteria which dictated the choice of the analytical methodology employed for the program samples were the intrinsic interferences of the technique, the error incurred during the implementation of the methodology and the availability of the required instrumentation.

A comparison of analytical results utilizing the aforementioned methodologies for chlorine and bromine determinations in oils, as presented in Reference 23, was considered in the choice of analytical protocols for the program samples. The methodology chosen for the program was a modified ASTM D 808-63. The modification of the procedure was basically the utilization of Ion Chromatography (IC) as the quantitative tool rather than the specified silver halide gravimetric determination. This would allow for the specificity required to distinguish the individual halide concentrations. In addition, IC eliminates the possible interference of high metals concentrations. The only known interference in the IC quantitative technique is the masking of analyte peaks of interest by high concentrations of other constituents having similar retention times.

Sample Preparation and Analysis

The oil samples were prepared and analyzed according to the Standard Operating Procedure (SOP), Total Halogen Analysis of Oils, as presented in Appendix B. The samples were initially homogenized by vigorously shaking the closed sample container prior to aliquoting. The physical observations noted for the program samples are illustrated in Table 11. Certain samples were extremely viscous and thus homogenization under closed conditions was not possible. Warming of the samples to improve flow for homgenization was discounted due to possible loss of volatile constituents prior to the analysis. The D 808-63 protocol called for samples containing in excess of 2 percent chlorine to be diluted with white oil, mineral oil, before combustion. No program samples were in excess of this level, therefore all sample aliquots taken were approximately 1g. Multiple aliquots of randomly chosen samples were taken for replicate analysis. Each replicate aliquot was removed from the freshly homogenized sample within 1/2 hour of the previously taken aliquot. The bomb was prepared according to the procedure outlined in the SOP. The sample was aliquoted into the clean cup and positioned in the bomb so that the thread dipped into the sample. After the secure assemblage

TABLE 11. PHYSICAL OBSERVATIONS OF PROGRAM OIL SAMPLES

Sample ID	GCA Control No.	Color	Other
12010-NJ-6-terminal	29642	Dark brown	Sample was solid mass, faint oil odor.
16375-NJ-6-terminal	29643	Dark brown	Viscous, fuel oil odor.
16379-NJ-4-terminal	29646	Dark brown	Viscous, fuel oil odor.
19028-NJ-6-terminal	29649	Dark brown	Viscous, fuel oil odor.
19190-NJ-6-refinery	29652	Dark brown	Viscous, strong odor.
20327-NJ-6-refinery	29656	Dark brown	Viscous, fuel oil odor.
20328-NJ-2-refinery	29657	Golden	Viscous, kerosene odor.
22621-NJ-4-terminal	29659	Dark brown	Very viscous, obvious pressure built up in container.
CE156A-NJ-4-terminal	29661	Dark brown	Viscous, little odor.
Site 9-NY-waste	29665	Light brown	Oil odor, crankcase oil.
Site 20-NY-waste	29669	Purple	Thin but lumpy, paint thinner odor.
WH188A-NJ-waste oil	29676	Dark brown	Little odor, very viscous, bottom residue present.
9-121-12-10-82-4-NYC-apartment	29679	Dark brown	Two phase, thick bottom residue.

of the bomb, oxygen was slowly admitted so as not to disturb the sample. The bomb (400 to 450 ml capacity) was pressurized to 30 atm. Subsequently, the bomb was placed in a cold water bath where the circuit was closed and the sample ignited. The bomb remained in the water bath for a minimum of 10 min., after which it was opened and the contents were examined for complete combustion. No program samples required recombustion. The collection of the sample for halide analysis was accomplished by successive small volume rinses of the interior of the bomb, bomb cover, and sample cup into a 600 ml beaker. The sample was covered with a speedyvap, placed on a hotplate, and the volume reduced to approximately 75 ml. The reduced sample was subsequently quantitatively transferred to a 100 ml volumetric for quantitation by IC. Before another sample was prepared for combustion, the Parr Bomb was scrubbed with hot soapy water and deionized water rinsed. The sample cup was cleaned by polishing with 400 grit emery paper followed by hot soapy water scrubbing and deionized water rinsing.

In addition to the preparation of the program samples and replicate aliquots of the program samples, mineral oil (designated method blank by D 808-63), mineral oil/organo-halogen spikes, carbonate collection solution, and program sample/organo-halogen oils were carried through the bomb procedure. Replicate carbonate collection solution aliquots (10 ml) were also prepared for halide analysis by carrying the carbonate through the procedure without the firing of the bomb.

The quantitation of total halogens as their halides was accomplished by utilizing a Dionex Model 14 Ion Chromatograph (IC). The instrument was set up according to the manufacturer's instructions. The columns in place for the analysis of the program samples were fast run anion precolumn, fast run anion separator, and fiber suppressor. The sample injection loop capacity was 100 μl. The eluent utilized was 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. The system was operated at a flow rate of 138 ml/hr. Prior to the analysis of program samples, calibration standards, prepared as outlined in the SOP, and laboratory control samples (LCS), as discussed in Section 7, were analyzed. No analyses of program samples were carried out until the reported halide concentrations for the LCS samples were verified as correct with the laboratory QC Coordinator. The aqueous detection limits for the halides as determined by standard calibration chromatograms, assuming 1 percent scale at 100 μmho setting, are 0.2 μg/ml for chloride as stated in the QA Plan (Appendix E), and 2 μg/ml and 0.2 μg/ml for bromide and fluoride, respectively. Sample analysis involved the injection of the originally prepared concentration and a ten-fold dilution. Sample chromatograms were compared to those of the aqueous calibration standards for quantitation. Where there was a question as to the relative retention time of the analyte in a sample versus the standards, the sample was reanalyzed with an aqueous spike of the analyte of interest to confirm correct peak identification.

This is illustrated in Figures C-1, C-2 and C-3 of Appendix C. Figure C-1 is the calibration standard chromatogram for 20 μg/ml Br^-, 5 μg/ml Cl^-, and 5 μg/ml F^-. The chloride retention time is 2.4 minutes which appears at 1.2 cm in Figure C-1. Figure C-2 is the chromatogram for 20328-NJ-2-refinery

(GCA 29657). There are two peaks in the vicinity of 1.2 cm, i.e., 1.15 and 1.45. The chromatogram presented in Figure C-3 is the 20328-NJ-refinery combustate diluted 1:1 and spiked with an aqueous chloride standard to contain 10 μg/ml in the final solution. This clearly defines the 1.15 cm peak as Cl^-.

All determinations of chloride for the samples were based upon the quantitation of the 1.15 cm peak. There was no incidence of coeluting or masking concentrations of other constituents relative to the determination of Cl^-. The reported values were calculated according to the SOP (Appendix B) where the blank value applied was the mean of the fired carbonate collection solution (Figure C-4). The issue of an appropriate blank value for this methodology is thoroughly discussed in Section 7 of this report.

Interpretation of the calibration standard chromatograms, as represented by Figure C-1 (Appendix C), gave 0.7 cm and 2.65 cm relative retentions for fluoride and bromide, respectively. Confirmation of the peak utilized in the quantitation of Br- was accomplished by analyzing a mineral oil spiked at an approximate 15,000 mg/kg level. As exemplified in Figure C-5 (Appendix C), all chromatograms for samples analyzed at the original combustate concentration demonstrated coelution in the vicinity of the Br- peak. High concentrations of interfering anions eluted over a broad window thereby masking the Br- peak region. A two-fold dilution of a combustate, Figure C-6, was spiked to contain 10 μg/ml Br- in the final solution and analyzed to see if resolution of the bromide was possible, Figure C-7. The spike was completely masked by the two interfering constituents. Based upon the relative retentions of the interfering peaks, it was postulated that the masking constituents were nitrate and sulfate present in the combustates. An aqueous solution containing 400 μg/ml NO_3-, 400 μg/ml SO_4, and 200 μg/ml Br- was analyzed to see if a significant concentration of Br- could be discerned in the presence of high levels of nitrate and sulfate. There was no resolution of the Br- peak.

All program sample combustates were also analyzed at a tenfold dilution. The dilution of the samples narrowed the retention window of the interfering constituents and enabled quantitation of the 2.65 cm Br- peak. As illustrated by Figure C-8, there was no peak present at the 2.65 cm retention for any of the program samples. Figure C-9 demonstrates the lowest limit of detection by aqueous standard curve comparison for this matrix utilizing a spiked mineral oil. This solution detection limit is equivalent to 600 mg/kg in the mineral oil.

There were no coelution or masking interferences evidenced in the F^- determinations. The high blank values analyzed for all categories, i.e., carbonate collection solution, carbonate collection solution contacted/not fired, carbonate collection solution fired, and mineral oil, appeared to be attributable to the carbonate collection solution (Section 7). Based upon the levels associated with the blank and the poor precision noted, a working detection limit of 0.5 μg/ml solution (twice the aqueous detection limit) or 50 mg/kg oil was assigned.

INORGANIC CHLORIDE IN OIL AQUEOUS EXTRACTION

Introduction

There are currently no available quantitative methodologies for the analysis of inorganic chloride in oil matrices. ASTM D 878-65, Reference 24, Inorganic Chlorides and Sulfates in Insulating Oils, is a qualitative procedure involving hot aqueous extraction of the oil followed by spot tests to indicate the presence of chloride, by precipitation as silver chloride, and sulfate, by precipitation as barium sulfate. The extraction portion of this analysis was used for the program samples. Total organic halide analysis (TOX), Method 450.1 in Reference 25, is intended for the analysis of TOX in waters. The procedure affords differentiation of organic and inorganic halides by the preliminary adsorption of organic halogens on GAC columns followed by the removal of inorganics by washing with nitrate solution. The analytical determination is a microcoulometric titration of the combusted organic halides. This methodology affords no specificity towards the individual halogens and does not quantitate organic fluorines. This analytical technique is not readily transferable to sample matrices which are not significantly water soluble or miscible with water soluble solvents. At this time, the only current application of the Dohrmann DX-20 Total Organic Halide Analyzer System to oil matrices is the determination of total halides by direct boat injection.

As stated in the QA Plan, Appendix E, a modification of D 878-65 was employed for the analysis of inorganic halides in the program oil samples. The most significant modification to D 878-65 was the utilization of IC and TOX as analytical tools. It was hoped that the IC would allow for the determination and quantitation of bromide, chloride, and fluoride by the protocol. TOX analysis was applied to determine the extent of extraction of organics by the hot aqueous procedure. During the analysis of similar samples, nondissociative emulsions formed during the extraction of the oils. A suitable solvent of low water solubility was included in the modified procedure for all samples in order to diminish the possibility of emulsion formation.

Sample Preparation and Analysis

The program samples were carried through the procedure as outlined in the SOP, Appendix B. The extraction carried out was two step, rather than the single step used in D 878-65, and maintained an extractant to sample ratio of 5:1 as opposed to 4:3, D 878-65. These procedural changes were implemented to favor high sample extraction efficiency. All sample aliquots, approximately 10g, were initially diluted with 20 ml 4-methyl-2-pentanone, methyl isobutyl ketone (MIBK). D 878-65 indicated the utilization of n-heptane as a solvent of dissolution of high viscosity samples such as polybutene. Dissolution of the program samples in n-heptane was unsuccessful. However, MIBK was found to be acceptable. After the sample was well mixed with MIBK, 25 ml hot deionized water was added to the centrifuge bottle. The sample was shaken, vented, and a second 25 ml hot deionized water aliquot added. The bottle contents were again shaken for approximately 5 min. Subsequently, the sample was centrifuged at a 55 dial setting, approximately 2500 rpm, for 10 min to achieve good phase separation. The aqueous phase was drawn off by pipet. The duplicate aliquotting of 25 ml hot deionized water followed by vigorous shaking was repeated, sample centrifuged, and aqueous phase drawn off and added to the first extract. The aqueous volume retrieved from the extraction was determined to indicate the completeness of the phase separation. Recoveries were in excess of 95 percent.

The aqueous extracts were analyzed by IC utilizing the same instrumental conditions as previously indicated. It was apparent that there were sufficiently high concentrations of MIBK in the aqueous extract to present gross interferences in this analytical technique. Figure C-10 aqueous extract 12010-NJ-6-terminal (GCA 29642), was typical of the sample extract chromatograms. Aqueous analyte spikes were performed for positive peak identification. The baseline decayed to an extent indicative of gross deleterious effects to column integrity making quantitation impossible. As a result of this unanticipated difficulty, the inorganic chloride concentrations were determined according to Method 325.2 of Reference 26. This involved the utilization of automated colorimetry. The aqueous extracts were analyzed according to the SOP, Appendix B, utilizing a Technicon Auto-Analyzer II System. Due to the degradation of IC columns and resultant difficulties, the determination of bromide and fluoride in the extracts was precluded.

The Dohrmann DX-20 was employed for the analysis of total organic halide analysis of the extracts. As stated in the QA Plan, Appendix E, this determination was performed to indicate the extent of extraction of organic halogens into the aqueous fraction. The analysis was carried out according to the protocol defined in Method 450.1, Reference 25.

The results of the inorganic chloride analysis would indicate that further methods work in this area is warranted. At present, the methodology must be considered semiquantitative at best. Due to the impossibility of spiking an oil matrix with an aqueous halide standard at a reliable level of confidence, no extraction efficiency value could be assigned to the determination.

The analysis of the oil fraction, after extraction, would not have provided useful information. The loss of volatile constituents was considerable due to the vigorous manipulation of the sample under the hot aqueous extraction conditions. Total halogens analysis would only have provided some value representative of both the remaining organics and the residual inorganics. The implementation of Method 450.1 for the program samples was precluded due to their low solubility in solvents such as methanol.

VOLATILE ORGANICS

Sample Preparation and Analysis

The oil samples selected for analysis for volatile organic compounds were extracted in tetraglyme and then analyzed by purge and trap gas chromatography/mass spectrometry (GC/MS). The sample preparative scheme was based upon Method A-101b of Reference 27 and incorporated protocols developed for a recently completed interlaboratory method evaluation study (Reference 28). The subsequent analyses were in accordance with Method 624 of Reference 29 with modifications as routinely implemented at GCA/Technology Division.

For sample preparation, a weighed aliquot (nominally 1 gram) of oil sample was extracted with tetraglyme (tetraethylene glycol dimethyl ether). The sample was mixed with 20 ml of precleaned tetraglyme and allowed to equilibrate in a 30 ml screw cap vial for a period of 12 to 18 hours. A portion of the tetraglyme layer was then withdrawn and stored in a screw cap vial with a minimum of headspace at 4°C. Quality control spikes which accompanied project samples through the preparation and analysis steps were prepared by spiking a stock mix of analytes into weighed aliquots of a representative waste oil of known volatile organic content. In addition, two oil samples were selected at random for replicate sample preparation. Three weighed aliquots of each were taken and extracted.

A measured portion of the tetraglyme extract was spiked into organic-free laboratory water for analysis by purge and trap GC/MS techniques. Details for the sample preparation and analyses are contained in the Standard Operating Procedures, "Volatile Organics: Tetraglyme Extraction with Modified 624 Analysis" and "Method 624: Volatile Organics Analysis" found in Appendix B.

Modifications to EPA Method 624 implemented for these analyses were as follows:

- A 25 ml sample was added to the purging chamber with a 30 ml syringe. Use of the larger purge chamber decreases the impact of the foaming typical of tetraglyme extracts and allows analysis of larger extract volumes than are possible in the specified 5 ml purge tube.
- The concentration of internal standard in each sample was reduced by a factor of five to prevent detector saturation.
- PFTBA was used for mass spectral tuning in place of BFB.
- The temperature program followed for the analysis was an initial temperature of 60° held for 4 minutes, then ramped at 10°/min to 220° and held.
- Stock mixes of standards were prepared in tetraglyme. These were spiked into laboratory water for calibration curve analysis.

Analyses were conducted on a Hewlett-Packard 5985 GC/MS interfaced to a Tekmar LSC 3 Liquid Sample Concentrator as described in the standard operating procedures (see Appendix B).

Standard reference materials of all analytes were used to prepare instrument calibration mixes. Serial dilutions of the compounds in tetraglyme were prepared in laboratory water and analyzed to establish calibration curves. These curves were generated on March 15, March 21, and April 7, 1983; all sample analyses were performed within 7 days of calibration curve analyses. One oil sample selected for volatile organics analysis was inadvertently omitted from the program at this time. It was extracted and analyzed at a later date with other oil samples under identical preparative and analytical protocols. On each day of sample analyses, EMSL standards mixed with tetraglyme were analyzed to validate instrument calibration. In addition, tetraglyme spiked into laboratory water was analyzed daily as a laboratory blank. Samples were corrected for the method blank analyzed on the same day as sample analysis. If any analytes were detected in the method blank, the area ratio measured for that compound relevant to the internal standard was subtracted from all sample results for that analyte prior to sample quantitation. Levels of analytes detected in method blanks analyzed with program samples ranged from <0.5 μg/l to a maximum of 5.8 μg/l. On the 3 days during which program samples with high levels of contamination were analyzed, two compounds, benzene and 1,1,1-trichloroethane were detected in the method blanks at levels ranging between 2.0 and 5.8 μg/l. These levels, attributed to system contamination, were used to correct the results for samples analyzed on these days. No other analytes were detected during the program in method blanks at greater than trace (2 μg/l) levels. Data for the calibration curve established March 15, 1983 and for a representative method blank are presented in Appendix C, pages 116 through 131.

The optimum volume of tetraglyme extract for analysis by these procedures depends upon the level of volatile organic compounds present in the oil sample. All oil samples of unknown content are initially assumed to contain volatiles at low (0.5 to 10) part per thousand levels of individual compounds. This in general avoids system contamination and mass spectrometer saturation by typical waste oil samples. Accordingly, a 10 to 20 μl aliquot of each tetraglyme extract was spiked into organic-free laboratory water for analysis. (The equation used to calculate extract volume for analysis is included in the Standard Operating Procedure cited above for tetraglyme analyses.)

All analyses of 10 to 20 μl aliquots of sample extracts were performed after system calibration and quality control analyses of EMSL spikes and method blanks. Data for these analyses were reviewed to establish the actual levels of volatile organic compounds present in the samples. The results of this review are summarized in Table 12, along with the consequent analytical decisions. At this time one of the two samples prepared in triplicate was selected for triplicate analysis. That sample containing the larger number of volatile organic components was chosen to provide precision data for the analyses.

As noted in Table 12, 15 of the 20 oil samples analyzed required a second analysis to provide data with minimum detection limits attainable on an individual sample basis. Data for the five oil samples containing volatiles within the assumed range were verified; no further analyses of these samples were performed, as the original analyses had been supported by all appropriate quality control measures, and no reduction of detection limits was possible.

Detection limits for these samples were based upon instrument sensitivity, method recoveries for the analytes, and sample size. The instrument sensitivity and method recoveries remain relatively constant for

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TABLE 12. VOLATILE ORGANICS ANALYSIS DATA REVIEW

Data review/assessment of volatile organic content and appropriate analytical response	Oil samples	GCA Control No.
Case 1: Volatile organic components were present in the 0.5 to 10 parts per thousand range in the oil sample. The 10 to 20 μl of extract purged provided maximum sensitivity; analysis of a larger aliquot would result in system overload by volatile components. The original analysis is therefore appropriate.	10683 CE 156A WH 187A WH 188A 9-121-12-10-82-4	29639 29661 29675 29676 29679
Case 2: Volatile organic compounds were present in the 0.5 to 10 parts per thousand range in the oil sample. A larger aliquot of tetraglyme extract could however be analayzed without seriously overloading the system. Lower detection limits are therefore possible; aliquots of 100 to 250 μl were analyzed.	20328 CE 158A ES 821203 ES 821204	29657 29663 29665 29666
Case 3: Volatile organic components were present in excess of 10 parts per thousand. Instrument saturation was noted for one or more compounds. Detection limits and quantitative results for all other analytes were based upon the original analysis of the 10 μl extract aliquot; reanalysis of a smaller aliquot was performed to allow accurate quantitation of the high level contaminants.	ES 821208 ES 821219 821219	29669 29670
Case 4: Volatile organic components were present in the oil sample at less than 0.5 parts per thousand. Larger extract aliquots (100 to 250 μl) were analyzed to provide maximum sensitivity towards all analytes in the samples.	10692 12010 16375 16379 19028 19190 20327 22621 22623	29641 29642 29643 29646 29649 29652 29656 29659 29660

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purge and trap gas chromatography/mass spectrometry procedures. Purge and trap recoveries for the halogenated and aromatic priority pollutant compounds are considerably higher than those noted for the highly soluble ketones and esters included as nonpriority pollutant analytes; as a direct result, detection limits for these nonpriority pollutants are greater. Detection limits for these analytes are further impacted by the oil sample matrix; the fragmentation patterns for the hydrocarbon ketones and esters produce ions also seen in the fragmentation of aliphatic hydrocarbons typical of oil samples. Against the oil background, relatively higher levels of the nonpriority pollutant esters and ketones must be present to be detected than in a water or tetraglyme standard sample.

The variability of detection limits for the oil sample analyses are a direct consequence of the analytical decision to provide the maximum information possible for each oil sample without compromising the instrument. Detection limits vary inversely with sample size; for samples with relatively low volatile organic content, a larger aliquot of tetraglyme extract could be spiked into water, purged, and analyzed, providing lower detection limits than possible for a heavily contaminated sample. It should be noted that nonanalyte volatiles were present in the majority of samples, and in many cases were the limiting factor for the analysis. These compounds were primarily homologous series of aliphatic hydrocarbons.

Detection limits for all samples are based upon an established instrument and method sensitivity of 10 ng for the priority pollutant compounds and the two nonpriority pollutant analytes, 1,1,2-trichloro-1,2,2-trifluoroethane and xylene. Detection limits for the ketones and esters for water samples and tetraglyme standards are normally 500 ng. With the adverse impact of the oil matrix, these limits for these analyses were conservatively established at 1000 ng. Quantitative values for compounds near their detection limits are less reliable; results are reported as "trace" when the amount of compound detected fell within 4 times the method detection limit. Calculations for resultant sample detection limits were performed by the equation as found in the Standard Operating Procedure for tetraglyme analyses.

The total ion chromatogram for a representative oil sample is found in Appendix C, Figure C-12. Data for this sample, including the calculation of detection limits, are presented on the accompanying pages.

SECTION 7

QUALITY ASSURANCE

INTRODUCTION

This section summarizes QA/QC activity on this project; subsections deal with Sampling QC, Laboratory Analysis QC, Performance and System Audits and Quality Problems and Corrective Actions. To limit the length of this section, most raw QC data (instrument calibration data sheets, custody forms, analysts' notebook pages, etc.) have been omitted. However, the Analytical QC subsection contains data reports for the QC samples specific to this project.

A combined Test/QA Plan was prepared in September 1982 and revised once; the current revision is dated February 1983. This section deals with the implementation of that Plan.

SAMPLING QUALITY CONTROL

GCA did not collect the project samples; Section 5 of this report briefly describes and references the sample collection procedures. The oil samples were received at ambient temperature in glass containers ranging in size from 40 ml to 1 liter. Most of the oil samples only partially filled their sample containers, leaving large volumes of air space within the containers. This condition would be favorable to the migration of volatile organic compounds into the existing air space or headspace. Thus, reported values for volatile organic compounds, including chlorinated organics, must be considered as minimum values.

Chain of Custody Procedures

On January 31, 1983, a set of 44 oil samples was delivered to the GCA/Technology Division Sample Bank in Bedford, Massachusetts. All samples were accompanied by chain of custody documentation; these records were signed by Sample Bank receiving personnel and entered in the permanent project file. Laboratory custody procedures as described in the QA Plan were followed.

Routine inspection upon receipt revealed all samples to be clearly identified and in good condition; there were no discrepancies between the sample labels and submitted sample custody records, and no breakage or leakage was noted. The submitted samples were entered in the Master Log Book and assigned individual GCA Control Numbers. The samples were received at ambient temperature and were stored in the room temperature Sample Bank.

At the time of receipt, a page for each sample was entered sequentially by GCA Control Number in the Custody Notebook, and the samples were transferred to the locked Sample Bank for storage until the time of analysis. Subsequent handling of the samples was documented by signed entries in the Custody Notebook. In addition, the transfer of samples between analysts within the laboratory was documented on Sample Custody Transfer forms which become part of the permanent project file and serve as a supplement to the Custody Notebook record of sample handling.

LABORATORY ANALYSIS QUALITY CONTROL

Quality Control (QC) protocols implemented for this program, as specified in the Quality Assurance Project Plan, included the use of method blanks, calibration blanks, duplicate samples and spiked samples. Blind quality control samples are normally submitted to the Sample Bank at the time of sample receipt and are assigned GCA Control Numbers so they are indistinguishable from project samples. Blind quality control samples were not submitted during this program for two reasons: (1) it was decided by the Laboratory QC Coordinator that the samples should not be split to submit blind duplicates; this was based on concerns regarding sample homogeneity and the possibility of loss of volatile organic halogens; (2) there was not immediately available a sufficient quantity of a well-characterized oil such as an NBS Standard Reference Material which could be submitted as an additional sample.

A brief synopsis of each control element is provided below. A more detailed discussion of each element, including results for each analytical category, is provided in subsequent portions of this section.

Blank Samples

Method Blanks--

Appropriate method blanks containing all reagents used in the preparation and analysis of samples were processed through the entire analytical scheme to assess spurious contamination arising from reagents, glassware and other materials used in the analysis. All reported data have been corrected by an appropriate method blank. Additional information regarding blanks used in the Parr Bomb procedure for the determination of total chlorine in oil is presented later in this section.

Calibration Blanks--

These are blanks which are used in instrument calibration and contain all reagents used in the preparation of calibration standards except the standard itself.

Laboratory Control Samples

Laboratory Control Samples (LCS) include both replicate samples and spiked samples (i.e., those fortified with predetermined quantities of the components of interest), which accompany program samples throughout the analytical scheme. Results from the analysis of control samples can provide information on analytical precision and accuracy.

Instrument Check Samples

These samples are usually prepared from an EPA/EMSL concentrate or other suitable reference material and are used on a daily basis to verify instrument calibration. Results from the analysis of these check samples are entered in the instrument logbook.

A summary of results for each of these quality control elements is provided in subsequent portions of this section.

Total Chlorine in Oil

Chlorine, measured as chloride, in project samples was determined using the procedures outlined in ASTM D 808-63 as stated in the QA Plan and described in Section 6 of this report. The only modification made to this procedure was the use of ion chromatography (IC) rather than gravimetric procedures to determine chloride in the combusted sample. The use of IC allows simultaneous determination of chloride, fluoride and bromide in the prepared sample.

Two types of blanks were analyzed. A mineral oil blank was used to correct the laboratory control samples which were prepared in mineral oil; the actual program samples were blank-corrected using data obtained from analysis of a series of sodium carbonate blanks. The sodium carbonate solution was placed in the bomb and the bomb was fired; the resulting solution was prepared and analyzed in the same manner as program samples. An average value generated from analysis of seven samples was used to correct project sample values. All blank data are presented in Tables 13 and 14.

All values obtained for total chlorine in mineral oil over the past 12 months are presented in Table 13. The values obtained for the oil designated "Lot No. 1" are high and variable; however, ASTM D 808 states that the blank value for mineral oil should not exceed 0.03 percent (300 mg/kg) chlorine, therefore, these values were not considered unusual. Data from a second bottle of mineral oil, designated Lot No. 2, are also presented. While this mineral oil was not used during this program, it does indicate that there may be significant variability in the chlorine content of U.S.P. mineral oil. Analysis of the samples received during this program represented an attempt to extend this method below the ASTM recommended range of 0.1 percent chlorine. The variability of the blank values becomes a significant factor when attempting to validate this method for low level chlorine samples.

Reported values for chloride in the sodium carbonate used as an absorbing solution in the Parr Bomb procedure are presented in Table 14. As shown in the table, the sodium carbonate solution was analyzed directly after preparation and after contact with the bomb. A 10 ml aliquot of sodium carbonate was placed in the bomb then rinsed out without firing the bomb, this is designated as "unfired" in Table 14. Another 10 ml aliquot was placed in the bomb and fired in the same manner as actual samples; this is designated as "fired" in Table 14. While there is not a significant difference between the

TABLE 13. QUALITY CONTROL RESULTS--REPORTED VALUES FOR MINERAL OIL BLANKS

Sample Identification	Bromine[c] (mg/kg)	Chlorine[d] (mg/kg)	Fluorine[e] (mg/kg)
Mineral Oil Lot No. 1[a]	< 600	252	452
		309	
		155	
		412	
		96	
		260	
		250	
		77	
		102	
		94	
Mean		201	
Relative Standard Deviation (%)		56	
Mineral Oil Lot No. 2[b]	< 600	<8	448
	< 600	14	465
Mean	< 600	--	457

[a] Mineral Oil, U.S.P. GCA Laboratory Lot No. 1 utilized for spiking purposes during analysis of program samples.

[b] Mineral Oil, U.S.P. GCA Laboratory Lot No. 2; these results are included for information purposes only.

[c] These values correspond to solution values of 6 μg/ml assuming a nominal 1.0g sample of mineral oil.

[d] These values correspond to solution values ranging from <0.08 to 4.12 μg/ml assuming a nominal 1.0g sample of mineral oil.

[e] These values correspond to solution values ranging from 4.48 to 4.65 μg/ml assuming a nominal 1.0 g sample of mineral oil.

TABLE 14. QUALITY CONTROL RESULTS--REPORTED VALUES FOR SODIUM CARBONATE BLANKS

Sample Identification	Bromide (µg/ml)	Chloride (µg/ml)	Fluoride (µg/ml)
Sodium Carbonate Reagent Blank[a]	<0.5	<0.08	5.31
	<0.5	<0.08	5.10
Sodium Carbonate Blank-Unfired[b]	<0.5	0.16	4.61
	<0.5	0.46	4.62
	<0.5	0.40	--
	<0.5	0.60	4.54
	<0.5	0.46	--
Mean	<0.5	0.42	4.59
Sodium Carbonate Blank-Fired[c]	<0.5	0.30	--
	<0.5	0.45	4.60
	<0.5	0.59	--
	<0.5	0.40	4.58
	<0.5	0.42	--
	<0.5	0.27	4.50
	<0.5	0.29	--
Mean	<0.5	0.39	4.56

[a] Direct analysis of reagent.

[b] Sodium carbonate solution was allowed to contact bomb interior but bomb was not fired.

[c] Sodium carbonate solution was placed in bomb and bomb was fired in the same manner as actual samples.

fired and unfired sodium carbonate blanks, the average value for the fired blanks was used to correct sample values since it more closely approximated conditions to which the samples would be subjected during preparation.

Replicate analyses were performed on three samples; these results are presented in Table 15. Aliquots of mineral oil and a project sample (19190-NJ-6-Refinery, GCA No. 29652) were spiked with known quantities of chlorinated organic compounds and subjected to the Parr Bomb preparation in order to assess procedural accuracy; these results are presented in Tables 16 and 17.

Prior to analysis of project samples, instrument calibration was verified by analysis of an EPA/EMSL quality control sample, (WP478-3). The expected value was 20.5 μg/ml chloride, the reported value was 21.6 μg/ml chloride, a recovery of 105 percent.

In addition to the Parr Bomb/IC technique, all project samples were analyzed for chlorine content using X-ray fluorescence (XRF). The samples were analyzed in duplicate, the reported XRF values shown in Table 18 represent the average of the duplicates. With the exception of two samples (GCA Nos. 29643 and 29652) there is reasonable agreement between the two sets of results. The discrepancy between reported values noted for the two samples was not pursued; the XRF values are presented for information purposes only and precision and accuracy estimates have not been provided for these measurements.

Total Fluorine in Oil

Total fluorine in oil was determined using the Parr Bomb/IC procedures used in the determination of total chlorine. High blank values presented a significant problem to this analysis. However, the sodium carbonate solution appeared to represent the major source of contamination. These results are presented in Tables 13 and 14. Samples of mineral oil and a project sample were spiked with fluorobenzene and analyzed using the Parr Bomb/IC procedure; these results are presented in Table 19. Three samples were analyzed in duplicate, the results are shown in Table 20. Prior to analysis of project samples, an EPA/EMSL quality control concentrate was analyzed to verify instrument calibration. The expected value for WP478-3 was 0.63 μg/ml fluoride; the reported value was 0.61 μg/ml, a recovery of 97 percent.

Total Bromine in Oil

Total bromine analysis was also performed using the Parr Bomb/IC protocols. However, significant quantities of sulfate and nitrate in the project samples masked the bromide peak and precluded quantitation of this parameter below a level of 600 μg/g. A project sample and aliquots of mineral oil were spiked with known quantities of brominated organic compounds at levels greater than 600 μg/g and analyzed in the same manner as project samples, these results are presented in Table 21. Replicate analyses were performed on three samples. These results are presented in Table 22. Instrument calibration was verified by analysis of an independently prepared

TABLE 15. QUALITY CONTROL RESULTS--REPLICATE ANALYSIS OF OIL SAMPLES FOR TOTAL CHLORINE

Sample Identification	GCA Control No.	Reported Values (chlorine mg/kg)							
		A	B	C	D	$\overline{X}$	S_x	Relative Standard Deviation (%)	Percent Difference
12010-NJ-6-Terminal	29642	750	787	773	763	768	16	2.1	--
20327-NJ-6-Refinery	29656	82	65	--	--	74	--	---	23
WH-188A-NJ-Waste Oil	29676	1,300	1,300	--	--	1,300	--	---	0

TABLE 16. QUALITY CONTROL RESULTS--ANALYSIS OF SPIKED MINERAL OIL FOR TOTAL CHLORINE

Sample Identification	Chlorine (mg/kg)[a] Reported	Expected	Percent Recovery
QC-1	231	229	101
QC-2	219	229	96
QC-3	1,200	1,440	83
QC-4	510	596	86
QC-5	479	577	83
Average Percent Recovery			90

[a]Samples were spiked with chlorodibromomethane.

TABLE 17. QUALITY CONTROL RESULTS--ANALYSIS OF SPIKED SAMPLE FOR TOTAL CHLORINE

Sample Identification	GCA Control No.	Chlorine[a] (mg/kg) Reported	Expected	Percent Recovery
19190-NJ-6-Refinery	29652	2,520	2,800	90
		787	914	86

[a]Samples were spiked with chlorobenzene.

TABLE 18. QUALITY CONTROL RESULTS--COMPARISON OF PARR BOMB/IC AND XRF DATA FOR TOTAL CHLORINE

Sample Identification	GCA Control No.	Reported (mg/kg)[a] Parr Bomb/IC	Reported (mg/kg)[a] XRF[a]
12010-NJ-6-Terminal	29642	768	750[b]
16376-NJ-6-Terminal	29643	149	1,630[c]
16379-NJ-6-Terminal	29646	99	60[b]
19028-NJ-6-Terminal	29649	81	ND[d]
19190-NJ-6-Refinery	29652	86	2,740
20327-NJ-6-Refinery	29656	74	ND[d]
20328-NJ-2-Refinery	29657	72	ND[d]
22621-NJ-4-Terminal	29659	81	ND[d]
CE 156A-NJ-4-Terminal	29661	1,360	2,360
Site 9-NY-Waste	29665	2,760	2,290
Site 20-NY-Waste	29669	13,400	10,200
WH 188A-NJ-Waste Oil	29676	1,300	870[b]
9-121-12-10-82-4-NYC-Apartment	29679	5,560	5,490

[a] Replicate values have been averaged; all XRF values represent an average of duplicate analyses.

[b] These values are below the optinum working range recommended for the instrument.

[c] A spike into the matrix showed an average recovery of 170 percent.

[d] Not detected.

TABLE 19. QUALITY CONTROL RESULTS--ANALYSIS OF SPIKED SAMPLES FOR TOTAL FLUORINE

Sample Identification	GCA Control No.	Fluorine (mg/kg) Reported	Expected	Percent Recovery
20328-NJ-2-Refinery	29657	103	160	64
Mineral Oil	---	127	225	56
		122	225	54

TABLE 20. QUALITY CONTROL RESULTS--REPLICATE ANALYSIS OF OIL SAMPLES FOR FLUORINE

Sample Identification	GCA Control No.	Reported Values (fluorine mg/kg) A	B	C	D	$\overline{X}$
12010-NJ-6-Terminal	29642	< 50	< 50	< 50	< 50	< 50
20327-NJ-6-Refinery	29656	< 50	< 50	--	--	< 50
WH 188A-NJ-Waste Oil	29676	< 50	< 50	--	--	< 50

TABLE 21. QUALITY CONTROL RESULTS--ANALYSIS OF SPIKED SAMPLES FOR TOTAL BROMINE

Sample Identification	GCA Control No.	Bromine (mg/kg) Reported	Expected	Percent Recovery
20328-NJ-2-Refinery	29657	10340	15390	67
Mineral Oil	---	600	1035	58
		600	1035	58

TABLE 22. QUALITY CONTROL RESULTS--REPLICATE ANALYSIS OF OIL SAMPLES FOR BROMINE

Sample Identification	GCA Control No.	Reported Values (bromine mg/kg) A	B	C	D	$\bar{X}$
12010-NJ-6-Terminal	29642	< 600	< 600	< 600	< 600	< 600
20327-NJ-6-Refinery	29656	< 600	< 600	--	--	< 600
WH 188A-NJ-Waste Oil	29676	< 600	< 600	--	--	< 600

standard, no EPA quality control samples were available for this parameter. The expected value for this sample was 27 μg/ml bromide, the reported value was 27.9 μg/ml, a recovery of 103 percent.

Inorganic Chlorides in Oil - Aqueous Extract

The oil samples were subjected to an aqueous extraction using procedures outlined in ASTM D 878-65 in order to determine whether the chlorine reported from the Parr Bomb/IC analysis was inorganic chloride. The extraction method is intended to be used as a qualitative test. It would not be possible to accurately spike an organic material such as the oils with an inorganic chloride in order to assess extraction efficiency. Consequently, these data should be regarded as minimum values.

Instrument calibration was verified by analysis of an EPA/EMSL quality control concentrate; WP 478-3 showed a recovery of 103 percent at the 20.5 μg/ml chloride level. In addition, an aliquot of the aqueous extract of 20328 NJ-2-Refinery (GCA No. 29657) was spiked to contain 5 μg/ml chloride; the reported value was 5.1 μg/ml, a recovery of 102 percent. A method blank was analyzed in the same manner as project samples; this sample did not contain measureable levels of chloride.

Total Organic Halides (TOX) Aqueous Extract

The water extracts obtained using the procedures described in the previous section were also analyzed for total organic halides in order to determine whether significant quantities of organics were also extracted. A deionized water sample spiked with 25.0 μg/g chloride, as trichlorophenol, was analyzed with project samples; the reported values for this sample were 25.8 μg, 25.0 μg and 24.2 μg TOX (reported as chloride). The calculated average percent recovery was 100 percent with a relative standard deviation of 3.2 percent.

Volatile Organics in Oil

Analysis of project samples for volatile organics was performed according to procedures defined in the Quality Assurance Plan and described in Section 6 of this report. Samples were corrected for the method blank analyzed on the same day as sample analysis. If any analytes were detected in the method blank, the area ratio measured for that compound relevant to the internal standard was subtracted from all sample results for that analyte prior to sample quantitation. Levels of analytes detected in method blanks analyzed with program samples ranged from <0.5 μg/l to a maximum of 5.8 μg/l. Benzene and 1,1,1-trichloroethane were detected on three of the days of program analyses at levels ranging between 2.0 and 5.8 μg/l. The detection of these analytes in method blanks appears to have been a result of system contamination due to analysis of samples containing high levels of volatile organics. No other analytes were detected during the program in method blanks at greater than trace (2 μg/l) levels. Representative blank results are presented in Appendix C of this report.

Instrument calibration was verified daily by analysis of an EPA/EMSL quality control sample; these results were entered in the instrument logbook. Representative data for the instrument check samples are presented in Table 23. Surrogates were not added to the samples during this program. As sample contamination varied widely, appropriate levels for surrogate spiking prior to extraction could not be determined. Surrogate addition immediately prior to analysis was not done; area responses for the three internal standards (as provided in Table 24) were monitored instead to establish the validity of each analysis. Quality control data generated for other programs where surrogates have been used support the reliability of internal standard areas as an alternative check. Each sample was spiked with a series of internal standard compounds prior to analysis. Representative extracted ion areas obtained for each of these compounds are presented in Table 24. These results were used to monitor the behavior of actual components in individual samples during the entire analysis scheme. A single sample, Site 20-NY-Waste (GCA No. 29669) was analyzed in triplicate for volatile organics; these results are presented in Table 25. Samples of a well-characterized and clean oil routinely used for quality control purposes were spiked with a number of components of interest and carried through the entire analytical procedure; these results are presented in Table 26. Table 27 presents results of quality control samples prepared for another project but analyzed by the same analytical protocols within the same time frame.

Discussion

Deviations from QA Plan--

The following deviations from the QA Plan have been noted for Analytical Laboratory Activities:

1. The Hewlett-Packard 5985 GC/MS rather than the Model 5993 was used for all volatiles analysis.

2. A Technicon Autoanalyzer II was used instead of the ion chromatograph to quantitate chloride in the aqueous extracts. Bromide and fluoride could not be quantitated in the aqueous extract of the oil since the IC was not used for analysis of these samples.

3. Minor modifications in instrument operating conditions and analytical procedures are noted in Section 6.

4. NBS Standard Reference Materials were not used in performance audits since appropriate SRMs were not available. EPA quality control materials and samples prepared internally were used to monitor the work.

5. Analytical quality control data were not presented in monthly reports to EPA.

6. Percent difference calculated as:

$$100 \left(\frac{\text{Reported Value 1 - Reported Value 2}}{\text{Average Reported Value}} \right)$$

TABLE 23. QUALITY CONTROL RESULTS--INSTRUMENT CHECK SAMPLES FOR VOLATILE ORGANICS

Compound	Concentration (µg/l)							
	A		B		C		D	
	Reported	Expected	Reported	Expected	Reported	Expected	Reported	Expected
Methylene chloride	48	40	Not spiked		19	20	22	24
Chloroform	49	49	160	180	28	25	29	29
1,2-dichloroethane	Not spiked		Not spiked		15	13	15	15
1,1,1-trichloroethane	40	50	15	17	25	25	29	30
Carbon tetrachloride	20	27	36	37	13	14	14	16
Bromodichloromethane	18	19	12	12	9.5	9.5	12	12
Dibromochloromethane	Not spiked		35	30	15	15	14	18
Trichloroethene	42	50	14	13	24	25	28	30
Bromoform	Not spiked		45	42	14	14	17	17
Tetrachloroethene	31	40	24	22	18	20	21	24
Chlorobenzene	26	40	Not spiked		20	20	22	24
Benzene	25	25	49	60	Not spiked		Not spiked	
Ethylbenzene	9.0	9.0	Not spiked		Not spiked		Not spiked	
Toluene	4.6	3.0	Not spiked		Not spiked		Not spiked	

TABLE 24. QUALITY CONTROL RESULTS--EXTRACTED ION AREAS FOR INTERNAL STANDARDS, VOLATILE ORGANICS ANALYSIS

Sample Identification		GCA Control No.	Bromochloromethane (128)	2-Bromochloro-propane (77)	1,4-Dichlorobutane (55)
Tetraglyme Standards	2 μg/l		511	1,765	352
	10 μg/l		678	1,884	391
	50 μg/l		473	1,751	341
	100 μg/l		513	2,040	412
	200 μg/l		534	2,093	398
10683-NJ-2-Terminal		29639	502	1,788	293
19028-NJ-6-Terminal		29649	557	1,880	403
19190-NJ-6-Refinery		29652	551	1,940	394
20327-NJ-6-Refinery		29656	542	1,903	356
10692-NJ-6-Terminal		29641	654	1,929	345
12010-NJ-6-Terminal		29642	513	1,770	366
16375-NJ-6-Terminal		29643	518	1,837	358
16379-NJ-6-Terminal		29646	538	1,807	305
22621-NJ-4-Terminal		29659	687	2,033	313
22623-NJ-6-Terminal		29660	719	2,126	380
CE156A-NJ-4-Terminal		29661	747	2,203	217
CE158A-NJ-4-Terminal		29663	762	2,278	b
Site 9-NY-Waste		29665	743	2,166	307
Site 10-NY-Waste		29666	709	2,091	513
Site 20-NY-Waste		29669A	793	2,540	343
Site 20-NY-Waste		29669B	879	2,529	242
Site 20-NY-Waste		29669C	760	2,393	283
Fabric and Leather-NY		29670	796	2,459	433
WH187A-NJ-Waste Oil		29675	786	2,409	374
WH188A-NJ-Waste Oil		29676	746	2,214	332
9-121-12-10-82-4-NYC-Apartment		29679	937	2,349	370
Site 20-NY-Waste		29669A	c	c	363
Site 20-NY-Waste		29669B	c	c	414
Site 20-NY-Waste		29669C	c	c	334
Site 20-NY-Waste		29670	c	c	470
Tetraglyme Standards	10 μg/l		597	1,956	385
	100 μg/l		656	2,475	449
	200 μg/l		724	2,941	494
		29642	609	1,844	423
QC 412			699	2,031	296
QC 414			717	2,096	331
Mean ($\bar{X}$)			661	2,110	365
Standard Deviation			121	286	64.7
Relative Standard Deviation (%)			18	14	18

[a] Internal standards are spiked into 25 ml aqueous solutions to achieve a concentration of 25 μg/l; see Appendix B, pages 96 and 101.

[b] Internal Standard could not be measured due to interferences from sample components.

[c] Sample reanalyzed only to quantitate those compounds which saturated the mass spectrometer on initial analysis. Data were reduced for only the region involved.

TABLE 25. QUALITY CONTROL DATA-TRIPLICATE ANALYSIS OF SITE 20-NY-WASTE (GCA NO. 29669) FOR VOLATILE ORGANICS

Compound	Concentration (mg/kg)				Relative Standard Deviation, (%)
	29669A	29669B	29669C	$\overline{X}$	
Methylene chloride	690	690	820	730	10
Trichlorofluoromethane	Trace	Trace	Trace	---	--
Chloroform	120	130	130	130	4.6
1,2-Dichloroethane	73	88	68	76	14
1,1,1-Trichloroethane	1,300	1,400	1,500	1,400	7.1
Trichloroethene	400	470	470	450	9.0
Benzene	450	520	590	520	13
Tetrachloroethene	970	750	1,100	940	19
Toluene	59,000	52,000	70,000	60,000	15
Ethylbenzene	6,900	6,000	8,200	7,000	16
1,1,2-Trichloro-1,2,2-trifluoroethane	340	390	380	370	7.2
Acetone	11,000	9,700	11,000	11,000	7.1
Methyl isobutyl ketone	15,000	17,000	18,000	17,000	9.2
Xylene (isomers)	30,000	36,000	40,000	35,000	14
Butyl acetate	8,300	9,000	10,000	9,100	9.4
Methyl ethyl ketone	31,000	35,000	35,000	34,000	6.9

TABLE 26. QUALITY CONTROL RESULTS--ANALYSIS OF SPIKED OIL SAMPLES FOR NON-PRIORITY POLLUTANT VOLATILE ORGANICS

Compound	Expected (μg)	Recovered (μg)			Average Recovery (%)
		QC 412	QC 414	$\overline{X}$	
acetone	3,500	1,600	1,500	1,600	46
butyl acetate	640	570	600	590	92
ethyl acetate	4,500	3,400	3,300	3,400	76
methyl ethyl ketone	1,500	960	950	960	64
methyl isobutyl ketone	940	800	840	820	87
trichlorotrifluoroethane	390	260	260	260	67
o-xylene	820	660	690	680	83

TABLE 27. QUALITY CONTROL RESULTS[a]--ANALYSIS OF SPIKED OIL SAMPLES FOR PRIORITY POLLUTANT VOLATILE ORGANICS

	Concentration (mg/kg)								
	Chloroform			1,1,1-Trichloroethane			Trichloroethene		
Sample Identification	Reported	Expected	Recovery (%)	Reported	Expected	Recovery (%)	Reported	Expected	Recovery (%)
QC 357[b]	ND[c]	--	--	170	--	--	ND[c]	--	--
QC 358	2,900	3,300	88	2,800	3,900	72	3,200	4,100	78
QC 359	3,500	3,600	97	3,500	4,300	81	5,000	3,700	140
QC 360	3,400	3,700	92	3,600	4,400	82	3,700	3,800	97
QC 494	4,500	3,800	120	3,500	2,900	120	3,500	4,000	86
QC 495	5,500	4,400	130	4,500	3,400	130	4,200	4,700	89
QC 496	5,700	4,500	130	4,800	3,500	140	4,600	4,900	94
Average Recovery (%)			110			100			97

[a] All results, including % recovery, rounded to two significant figures.

[b] Background oil only. Background analysis results were used to correct spikes for any components native to the matrix.

[c] ND = 30 mg/kg.

[d] Component not spiked.

was used in place of standard deviation and relative standard deviation in assessing precision when fewer than three measurements were available.

Precision, Accuracy and Completeness

A summary comparison of the goals for precision, accuracy and completeness stated in the QA Plan with the results achieved is presented in Table 28. Precision has been estimated from the results achieved in the analysis of replicate project samples and quality control samples. The values presented are averages; for example, precision for the volatile organics can be compound specific, a given compound may exhibit slightly better or worse precision than the value presented. Precision has been estimated from the relative standard deviation (for three or more measurements) or percent difference (for duplicate analyses).

Accuracy has been estimated from the analysis of spiked program samples and quality control samples containing known concentrations of the parameters of interest. Again, the accuracy presented must be considered an average for a given category. The overall accuracy for the priority pollutant volatiles achieves the goal of ±20 percent; the overall accuracy for the non-priority pollutant volatiles is ±30 percent.

Estimates of accuracy for the bromine and fluorine results have been provided for high level spikes and may not reflect the accuracy associated with analyses at or approaching detection limits.

Completeness, as defined in the QA Plan, is the percentage of measurements considered valid out of the total number of measurements made. The following validation criteria were used in assessing data generated during this program.

- Use of properly operating and calibrated equipment.
- Use of appropriate analytical procedures.
- Adherence to required quality control procedures.
- Precision and accuracy achieved comparable to that achieved in similar analytical programs.

Based on these requirements, the data obtained during this program have been judged valid. However, certain precautions must be added. The samples, as stated in the QA Plan, had been analyzed prior to receipt at GCA; therefore, considerable headspace existed in some containers. As a result, the values reported for volatile organics and the halogens must be viewed as minimum values.

The quality control results for the fluorine analysis indicate recoveries on the order of 50 to 60 percent; therefore, when actual values are reported for this parameter they should be considered minimum values.

TABLE 28. QUALITY CONTROL RESULTS-PRECISION, ACCURACY AND COMPLETENESS

Measurement	Precision (%)			Accuracy (%)			Completeness (%)	
	Goal	Achieved	Result table	Goal	Achieved	Result table	Goal	Achieved
Oils								
Volatile Organics	25	20	25	±20	c	26, 27	95	100
Total Chlorine	10	>200 mg/kg, 10 <200 mg/kg, 25	15	±20	±20	16, 17	95	100
Total Bromine	10	b	22	±20	±50	21	95	100
Total Fluorine	10	b	20	±20	±50	19	95	100
Aqueous Extract								
Total Halides (TOX)[a]	10	10	d	±20	±20	d	95	100
Chloride	Not provided	Not assessed	--	Not provided	Not assessed		Not provided	Not assessed
Bromide	Not provided	Not analyzed	--	Not provided	Not analyzed		Not provided	Not analyzed
Fluoride	Not provided	Not analyzed	--	Not provided	Not analyzed		Not provided	Not analyzed

[a] Instrumental analysis only.

[b] These values are generally below detection limit and are not useful in assessing analytical precision.

[c] The accuracy for the volatile organics is highly compound specific. Overall accuracy for the priority pollutant volatiles is generally within 20%. Accuracy for the non-priority pollutant volatiles is generally on the order of ±30%.

[d] Presented in text.

The variability associated with the mineral oil blanks and the poorer precision (± 25 percent) observed in replicate analyses at low levels for total chlorine analyses should be considered when assessing results below approximately 200 mg/kg.

PERFORMANCE AND SYSTEM AUDITS

Laboratory Analysis Performance Audits

As noted earlier, blind QC samples prepared from project samples and indistinguishable to the analyst from project samples could not be prepared for this project. However, several sets of QC samples prepared at GCA by spiking compounds of interest into an oil matrix served to audit the accuracy of the analytical work. Although identified as QC samples, their concentrations were not known to the analyst. Table 29 indicates the table in this section which summarizes results on these samples.

TABLE 29. QC SAMPLES SERVING AS PERFORMANCE AUDITS

Measurement	Result Table
Total Chlorine	16, 17
Total Fluorine	19
Total Bromine	21
Volatile Organics	26, 27

System Audit

A system audit is an overall evaluation of a project to check on the use of appropriate QC measures and ensure that the quality system planned for the project has been implemented. Such an audit was not conducted during the active analytical work. During the week of July 5, 1983 the QA Manager audited the project by reviewing analytical data and the draft final report against the QA Plan. A written audit report was not prepared but the audit results are essentially presented in this section.

External Audit

A system audit of this project was conducted by EPA and RTI personnel on July 13 and 14, 1983.

QUALITY PROBLEMS AND CORRECTIVE ACTIONS

The QA Manager's review of analytical raw data indicated that existing data on Parr Bomb mineral oil blanks from other projects should be compiled and new data on sodium carbonate blanks should be gathered. This has been done and presented in this section. The mean sodium carbonate blank value has been used to correct project samples.

Degradation of the ion chromatograph columns which may have been caused by MIBK in the aqueous extract prevented the analysis of the extract for chloride, bromide and fluoride. The corrective action taken was to use the Technicon Autoanalyzer for chloride analysis of the extract; an alternate analytical technique was not available for bromide and fluoride.

SECTION 8

DISCUSSION OF RESULTS

VOLATILE ORGANIC COMPOUNDS

The conditions of the samples must be considered when discussing the results for volatile organic analyses. EPA Method 624 which is normally applied to water samples containing volatile species at concentrations of 0.005 to 1.0 ppm specifies that these samples will be collected in hermetically sealed vials, stored at 4°C and analyzed within 14 days. It would be a good practice to apply the same criteria to oil samples, as GCA planned to do. However, as noted in the QA plan, GCA did not collect the samples and had no control over sample collection or preservation. Therefore, GCA had to analyze samples that were collected in 1 quart jars that had been partially analyzed. In addition, as discussed in Section 4 these samples had been stored for several months and flown from the east to the west coast and back. The effect of sample handling and storage on the results of this program are speculative as no investigation and analysis of these conditions have been conducted.

There are two important differences between the analyses conducted under this program and the analysis of water samples. First, the volatile organic concentrations in water samples are in the 0.005 to 1.0 ppm (mg/kg) range while the levels of volatile organics that were investigated in this study were in the 1 to 95,000 ppm range. The percentage of volatiles lost at high concentrations should be less than at low concentrations. In addition, when the volatiles are in the 5 to 20 percent range, it is possible that water (boiling point 100°C) is as likely to be lost as some volatiles (toluene has a boiling point of 111°C).

A second difference is that oil samples, not water samples, were analyzed in this study. In general, the volatile components that were analyzed are much more soluble in oil than water and thus are much more likely to remain in the liquid phase. In addition, the higher viscosity of the oil could retard the loss of volatiles. In the extreme cases, some of the No. 6 oils are practically solid at room temperature. The diffusion of volatile organics to the surface can be expected to be a relatively slow process.

Despite the differences between this study and EPA Method 624 analyses of water, the possible significant loss of volatile organic compounds must be considered as a real possibility. The more volatile (higher vapor pressure or lower boiling point) compounds are the ones that are most likely to be lost. Boiling points for the 39 volatile organic compounds that were analyzed in this study are presented in Table 30.

Most of the 13 virgin oil samples that were analyzed contain detectable concentrations of benzene, ethylbenzene, toluene and xylene. Whether a compound is considered a harmful contaminant or not can depend on several criteria including its toxicity, concentration, combustion characteristics and ultimate impact on the environment. In this study we have simply tried to identify compounds that are either not expected to be present in virgin oils, such as many of the chlorinated solvents which are not a normal component of crude oil, or compounds that are present at high concentrations relative to the other oils. Considering the precision of the volatile analyses (± 25 percent), the questions about sample preservation, the possible differences between oils and the very limited data, statistical analyses do not appear to be warranted.

Because the four compounds in Table 31 are normal components of oil, it seems reasonable to assume that the lower levels reported represent typical uncontaminated oil. The possible alternative conclusion, that all samples except sample H are contaminated does not appear to be a reasonable possibility. Sample E contains high concentrations relative to the other No. 4 oils and the other virgin oils and should clearly be classified as contaminated. The results for sample N are also rather high and are good indications of contamination. Other possibilities for contaminated oil are Samples B, C, F, and K. Sample K contains high concentrations relative to the other No. 6 oils. Although the data are extremely limited, it suggests that the more volatile No. 2 oils may typically contain higher levels of benzene, ethylbenzene, toluene and xylene.

Data for all the volatile compounds that were detected in any oil sample are presented in Table 32 for the same 13 virgin oil samples. The data showing high (relative to the other oils) concentrations of methyl ethyl ketone, tetrachloroethene, 1,1,1-trichloroethane, and 1,1,2-trichloro-1,2,2-trifluoroethane in sample E confirm that this is a contaminated oil. It should be noted that statements such as "high" and "contaminated" do not necessarily imply harmful environmental effects.

Contamination of samples F and N is clearly confirmed by the presence of several chlorinated and fluorinated compounds not found in the other virgin oils.

Sample K may also be contaminated. It contains detectable concentrations methylene chloride (11 mg/kg), 1,1,1-trichloroethane (8 mg/kg) and trichlrofluoromethane (10 mg/kg) compared to undetectable (often less than 1 mg/kg) levels in many of the other oil samples.

Sample C which seemed to have marginally high concentration of benzene, ethylbenzene, toluene, and xylene does not have detectable levels of any of the other 35 compounds. It should probably not be classified as contaminated.

TABLE 30. VOLATILE ORGANIC COMPOUNDS THAT WERE ANALYZED AND THEIR BOILING POINTS

Compound	Boiling Point, °C
Chloromethane	-24
Dichlorodifluoromethane	-30
Bromomethane	4
Vinyl chloride	-13
Chloroethane	12
Methylene chloride	40
Acrolein	53
Acrylonitrile	79
Trichlorofluoromethane	24
1,1-dichloroethylene	37
1,1-dichloroethane	57
Trans-1,2-dichloroethylene	48
Chloroform	62
1,2-dichloroethane	84
1,1,1-trichloroethane	74
Carbon tetrachloride	77
Bromodichloromethane	90
Bis-chloromethyl ether	59
1,2-dichloropropane	96
Trans-1,3-dichloropropene	77
Trichloroethylene	87
Dibromochloromethane	119
Cis-1,3-dichloropropene	104
1,1,2-trichloroethane	114
Benzene	80
2-chloroethylvinyl ether	109
Bromoform	150
Tetrachloroethene	121
1,1,2,2-tetrachloroethane	146
Toluene	111
Chlorobenzene	131
Ethylbenzene	137
Acetone	56
Butyl acetate	125
Ethyl acetate	77
Methyl ethyl ketone	80
Methyl isobutyl ketone	117
1,1,2-trichloro-1,2,2-trifluoroethane	48
Xylene (isomers)	140

TABLE 31. BENZENE, ETHYLBENZENE, TOLUENE AND XYLENE CONCENTRATIONS IN VIRGIN OIL SAMPLES[a] (mg/kg)

Sample Identification	A	B	C	D	E	F	G	H	I	J	K	L	M	N
GCA Control No.	29639	29657	29646	29659	29661	29663	29641	29642	29643	29649	29660	29652	29656	29679
State or City Sample Code	10683	20328	16379	22621	CE 156A	CE 158A	10692	12010	16375	19028	22623	19190	20327	A[b]
Oil Grade	2	2	4	4	4	4	6	6	6	6	6	6	6	4
Compound / Oil Source	terminal	refinery	terminal	terminal	terminal	terminal	terminal	terminal	terminal	terminal	terminal	refinery	refinery	apartment
Benzene	<20	110	46	45	590	140	23	<2	15	30	37	28	15	< 100
Ethylbenzene	240	970	160	120	2,500	240	94	<2	47	30	230	110	21	580
Toluene	440	910	230	110	7,900	490	87	<2	49	40	330	110	100	730
Xylene (isomers)	590	4,100	110	79	7,900	160	67	22	47	36	180	50	20	1,900

[a] All samples are from New Jersey except 29679 which is from New York City.

[b] Sample from New York. Original sample code is 9-121-12-10-82-4.

TABLE 32. SUMMARY OF RESULTS OF VOLATILE ORGANIC ANALYSES OF VIRGIN OILS (mg/kg)

Compound / Sample Identification	A	B	C	D	E	F	G	H	I	J	K	L	M	N
GCA Control No.	29639	29657	29646	29639	29661	29663	29641	29642	29643	29649	29660	29652	29656	29679
State or City Sample Code	10683	20328	16379	22621	CE156A	CE158A	10692	12010	16375	19028	22623	19190	20327	A[a]
Oil Grade	2	2	4	4	4	4	6	6	6	6	6	6	6	4
Oil Source	terminal	refinery	terminal	terminal	terminal	terminal	terminal	terminal	terminal	terminal	terminal	refinery	refinery	apartment
Acetone	<2,000	<2,000	<100	<100	2,600	< 200	< 100	<200	<90	<100	<100	<100	<90	<2,000
Benzene	<20	<110	46	45	590	140	23	<2	15	30	37	28	15	<100
Butyl acetate	<2,000	<2,000	<100	<100	<1,000	< 200	< 100	<200	<90	<100	<100	<100	<90	<2,000
Chloroform	<20	<20	< 1	<1	<10	10	< 1	<2	<0.9	<1	<1	<1	< 0.9	<20
1,2-dichloroethane	<20	<20	< 1	<1	<10	<2	< 1	<2	<0.9	<1	<1	<1	< 0.9	<20
1,1-dichloroethene	<20	<20	< 1	<1	<10	49	<1	<2	<0.9	<1	<1	<1	< 0.9	<20
Ethylbenzene	240	970	160	120	2,500	240	94	<2	47	30	230	110	21	580
Methylene chloride	<20	<20	< 1	<1	<10	180	<1	<2	<0.9	<1	11	< 1	< 0.9	<20
Methyl ethyl ketone	<2,000	<2,000	< 100	<100	9,900	< 200	< 100	< 200	<90	< 100	< 100	< 100	< 90	< 2,000
Methyl isobutyl ketone	<2,000	<2,000	< 100	<100	<1,000	< 200	<100	< 200	<90	< 100	<100	< 100	< 90	< 2,000
Tetrachloroethene	<20	<20	< 1	<1	140	140	< 1	< 2	< 0.9	< 5	< 1	< 1	<0.9	< 20
Toluene	440	910	230	110	7,900	490	87	< 2	49	40	330	110	100	730
1,1,1-trichloroethane	<20	<20	<1	<1	950	1,900	< 1	< 2	< 0.9	<1	8	<1	<0.9	3,900
Trichloroethene	<20	<20	<1	<1	< 10	170	< 5	< 2	< 4	<1	< 1	<1	<0.9	< 20
Trichlorofluoromethane	<20	< 20	<1	<1	< 10	14	<1	<2	<0.9	<1	10	<1	<0.9	< 20
1,1,2-trichloro-1,2,2-trifluoroethane	<20	<20	<1	<1	< 40	26	<1	<2	<0.9	<1	< 1	<1	<0.9	< 20
Xylene (isomers)	590	4,100	110	79	7,000	0	67	22	47	36	180	50	20	1,900
Other compounds[b,c]	<20	<20	< 1	<1	< 10	< 2	<1	<2	<0.9	<1	< 1	<1	<0.9	< 0

[a] A sample code is 9-121-12-10-82-4. This is the only sample from New York. All others are from New Jersey.

[b] Results for compounds that were detected in any samples are presented in this table. See Appendix D for complete results.

[c] Not including acrolein and acrylonitrile which are less than 50 times the indicated value.

None of the other samples show any evidence of contamination.

In summary, four virgin oil samples (E, F, K, N) show indications of contamination by volatile organic compounds. Contaminants that were identified in one or more of these samples are acetone, benzene, chloroform, 1,1-dichloroethene, ethylbenzene, methylene chloride, methyl ethyl ketone, tetrachloroethene, toluene, 1,1,1-trichloroethane, trichloroethene, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and xylene. Caution should be used in interpreting the results due to possible loss of volatiles. Whether or not the contaminants that were identified lead to any environmental impacts depends on many factors not addressed in this study, such as toxicity and the effects of combustion on emissions.

Six waste oils were analyzed for 39 volatile organic compounds. The waste oils consisted of automotive wastes and industrial byproducts or wastes that may have included transformer oil, turbine engine lubricants, refrigeration lubricants, printing wastes, painting wastes, dry cleaning waste, chemical wastes and food processing industry wastes.

Results for the volatile organic analyses are presented in Table 33. Some of the New York wastes contain percentage quantities of various volatile organic compounds. These are believed to be industrial wastes. The two New Jersey samples are probably automotive waste oils. All the waste oils contain higher concentrations of volatile organic compounds than the uncontaminated virgin oils.

HALOGENS

Thirteen oil samples were analyzed for total bromine, fluorine and chlorine. Each sample was extracted with water to try to separate the inorganic chlorides from the oil. The water phase was analyzed for total chloride and total organic halogens. The analytical methods have been discussed in Section 6. Results of the analyses are presented in Table 34.

Most samples did not contain measureable concentrations of bromine or fluorine. Bromine concentration in all samples were below 600 mg/kg. With the exception of two samples (O and Q) fluorine concentrations were below 50 ppm. Samples O and Q, which were waste oil samples from New York that contained many volatile organic compounds, contained 96 and 182 mg/kg total fluorine as shown in Table 34.

Total chlorine concentrations were measured in ten virgin fuel oil samples (B-N). Six samples (B, C, D, J, L, M) from refineries and terminals had total chlorine concentrations in the 72 to 99 mg/kg. These six samples included No. 2, No. 4, and No. 6 oils and showed no evidence of contamination by volatiles. The other four samples had higher concentrations of 149 mg/kg (I), 768 mg/kg (H), 1,360 mg/kg (E) and 5,560 mg/kg (N). Only samples E and N showed any indication of contamination by volatile organic compounds (see Table 32).

TABLE 33. SUMMARY OF RESULTS OF VOLATILE ORGANIC ANALYSES OF WASTE OIL[a] (mg/kg)

Compound	Sample Identification GCA Control No. State or City Sample Code State	O 29665 Site 9 NY	P 29666 Site 10 NY	Q 29669 Site 20 NY	R 29670 Fabric and leather NY	S 29675 WH187A NJ	T 29676 WH188A NJ
Acetone		<700	<300	11,000	<2,000	< 2,000	< 2,000
Benzene		55	<3	520	<100	< 90	< 80
Butyl acetate		<700	<300	9,100	<2,000	< 2,000	< 2,000
Chloroform		<0.7	<3	130	<20	< 20	< 20
1,2-dichloroethane		8.4	<3	76	<20	< 20	< 20
1,1-dichloroethene		15	42	<10	<20	< 20	< 20
Ethylbenzene		190	50	7,000	3,900	630	800
Methylene chloride		15	<3	730	3,000	< 20	< 20
Methyl ethyl ketone		<700	<300	34,000	95,000	< 2,000	< 2,000
Methyl isobutyl ketone		<700	<2,000	17,000	18,000	< 2,000	< 2,000
Tetrachloroethene		39	3,500	940	21,000	490	310
Toluene		480	<3	60,000	81,000	1,300	1,800
1,1,1-trichloroethane		970	17	1,400	28,000	270	420
Trichloroethene		5.6	440	450	14,000	< 20	< 20
Trichlorofluoromethane		510	<3	< 40	<20	< 20	< 20
1,1,2-trichloro-1,2,2-trifluoroethane		< 0.7	<3	370	320	< 20	< 20
Xylene		110	93	35,000	19,000	2,700	3,300
Other compounds[b]		< 0.7	<3	< 10	<20	< 20	< 20

[a] Results are presented for all compounds that were detected in any samples. See Appendix D for complete results. These "waste oils" are generally not typical automotive waste oils and may include industrial wastes that are burned as fuels.

[b] Not including acrolein and acrylonitrile which are less than 50 times the indicated value.

TABLE 34. RESULTS OF HALOGEN ANALYSES (mg/kg)

Sample Identification	B	C	D	E	H	I	J	L	M	N	O	Q	T
GCA Control No.	29657	29646	29659	29661	29642	29643	29649	29652	29656	29679	29665	29669	29676
State or City Sample Code	20328	16379	22621	CE156A	12010	16375	19028	19190	20327	A^a	Site 9	Site 20	WH 188A
Oil Grade	2	4	4	4	6	6	6	6	6	4	Waste	Waste	Waste
Analyte / Oil Source	Refinery	Terminal	Terminal	Terminal	Terminal	Terminal	Terminal	Refinery	Refinery	Apartment	---	---	---
Total Bromine	< 600	< 600	< 600	< 600	< 600	< 600	< 600	< 600	< 600	< 600	< 600	< 600	< 600
Total Flourine	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	< 50	96	182	< 50
Total Chlorine	72	99	81	1,360	768	149	81	86	74	5,560	2,760	13,400	1,300
Water Extractable Chloride	< 8	44	20	187	936	101	44	27	44	140	580	1,620	72
Water Extractable Organic Halogens	0.043	0.15	< 0.06	1.6	0.38	< 0.05	< 0.06	< 0.092	< 0.065	0.92	1.7	134	1.65

The water extractable chloride concentrations in these ten virgin oil samples varied from 8 mg/kg to 936 mg/kg. Four samples contained less than 25 percent water extractable chlorides, two samples contained 25 to 50 percent and four samples contained more than 50 percent water extractable chlorides. The level of organic halogens in the water extracts were not significant. These results indicate that inorganic chlorides, as measured by the water extraction procedure, appeared to account for less than 50 percent of the total chlorine in the virgin oil samples.

Halogen results are also presented in Table 34 for three waste oil samples. Inorganic chlorides generally account for about 5 to 25 percent of the total chlorine in these samples.

Results of the volatile organic analyses and the halogen analyses are compared in Table 35 in order to present a more complete picture of the samples. Two of the virgin oil samples (E and N) show high levels of at least one chlorinated volatile organic compound. These two virgin oil samples also show high total chlorine levels and low percentages of inorganic chloride relative to the total chlorine level.

The other eight virgin oil samples did not contain detectable levels of volatile chlorinated organic compounds. Reference to Table 32 also shows that, except for sample B which was a distillate oil, the samples did not contain high levels of nonchlorinated volatile organic compounds. Sample C is fairly typical of the results for these eight virgin oil samples. Sample C does not show any evidence of volatile organic contamination. Inorganic chlorides account for a significant fraction but not all of the chlorine in the oil. Therefore, the sample may be contaminated by semivolatile chlorinated compounds, volatile chlorinated compounds that were not analyzed, or inorganic chlorides that were not completely extracted when the total chlorine was below 100 mg/kg. However, the unaccounted for chlorine may also be attributable to the precision (±25 percent) of the low level halogen analyses.

The three waste oil samples all show high levels of volatile chlorinated organic compounds. In these three samples, the volatile compounds account for 46 percent (O), 25 percent (Q), and 53 percent (T) of the total chlorine. When the inorganic chlorides are considered, the analyses accounted for 67 percent (O), 37 percent (Q) and 59 percent (T) of the total chlorine. The unaccounted for chlorine may reflect the precision of the analyses or may consist of semivolatile chlorinated organic compounds, volatile chlorinated compounds that were not analyzed or inorganic chlorides that were not extracted. Sample Q, in fact, has been recently reported to contain 3,150 mg/kg of PCBs.[15]

CONCLUSIONS

A small group of virgin fuel oil and waste oil samples was analyzed for 39 selected volatile organic compounds, chlorine, bromine, and fluorine. There may have been significant loss of volatile organic compounds prior to analysis by GCA because the samples were opened, partially analyzed under another project, and not maintained at 4°C in a headspace free condition.

TABLE 35. COMPARISON OF VOLATILE ORGANIC AND HALOGEN RESULTS (mg/kg)

Sample Identification	B	C	D	E	H	I	J	L	M	N	O	Q	T
GCA Control No.	29657	29646	29659	29661	29642	29643	29649	29652	29656	29679	29665	29669	29676
State or City Sample Code	20328	16379	22621	CE156A	12010	16375	19028	19190	20327	A^a	Site 9	Site 20	WH 188A
Oil Grade	2	4	4	4	6	6	6	6	6	4	Waste	Waste	Waste
Compound / Oil Source	Refinery	Terminal	Terminal	Terminal	Terminal	Terminal	Terminal	Refinery	Refinery	Apartment	---	---	---
Chloroform	<2	<1	<1	<10	<2	<0.9	<1	<1	<0.9	<20	<0.7	130	<20
1,2-dichloroethane	<2	<1	<1	<10	<2	<0.9	<1	<1	<0.9	<20	8.4	76	<20
1,1-dichloroethene	<2	<1	<1	<10	<2	<0.9	<1	<1	<0.9	<20	15	<10	<20
Methylene chloride	<2	<1	<1	<10	<2	<0.9	<1	<1	<0.9	<20	15	730	<20
Tetrachloroethene	<2	<1	<1	140	<2	<0.9	<5	<1	<0.9	3,900	39	940	310
1,1,1-trichloroethane	<2	<1	<1	950	<2	<0.9	<1	<1	<0.9	<20	970	1,400	420
Trichloroethene	<2	<1	<1	<10	<2	<4	<1	<1	<0.9	<20	5.6	450	<20
Trichlorofluoromethane	<2	<1	<1	<10	<2	<0.9	<1	<1	<0.9	<20	510	<40	<20
1,1,2-trichloro-1,2,2-trifluoroethane	<2	<1	<1	<40	<2	<0.9	<1	<1	<0.9	<20	<0.7	370	<20
Fluorine detected in volatiles	<2	<1	<1	<40	<2	<0.9	<1	<1	<0.9	<20	71	112	<20
TOTAL FLUORINE	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	96	182	<50
Chlorine detected in volatiles	<2	<1	<1	915	<2	<4	<5	<1	<0.9	3,100	1,260	3,300	690
Water extractable chloride	<8	44	20	187	936	101	44	27	44	140	580	1,620	72
TOTAL CHLORINE	72	99	81	1,360	768	149	81	86	74	5,560	2,760	13,400	1,300

Many of the samples were selected for analysis because they were suspected or known to be contaminated. The results provide examples of the types of compounds and indications of the concentrations that may be found in contaminated oil. Any generalizations about the extent of contamination or the concentrations of contaminants in virgin fuel oil or waste oil are not appropriate.

Thirteen virgin fuel oil samples were analyzed for 40 selected volatile organic compounds. Three samples from terminals (E, F, and K) and one from an apartment house (N) were contaminated with volatile organic compounds. Contaminants that were identified in one or more of these samples are acetone, benzene, chloroform, 1,1-dichloroethane, ethylbenzene, methylene chloride, methyl ethyl ketone, tetrachloroethene, toluene, 1,1,1-trichloroethane, trichloroethene, trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane and xylene. Concentrations were in the range from 10 to 10,000 mg/kg range.

Seven waste oil samples were also analyzed for volatile organic compounds. These samples may have included automotive waste oils and industrial chemical wastes that are apparently burned as fuel in New York. All the waste oil samples were contaminated with volatile organic compounds. Seventeen compounds with concentrations in the 6 to 95,000 mg/kg range were identified in one or more samples.

Ten of the previously discussed virgin fuel oil samples were analyzed for total chlorine, bromine and fluorine. Bromine concentrations were below 600 mg/kg and fluorine concentrations were below 50 mg/kg in all samples. Two samples that were previously identified as being contaminated with volatile organic compounds contained 1,366 and 5,560 mg/kg total chlorine. Seven samples not contaminated with volatile organic compounds contained 72 to 146 mg/kg total chlorine while one sample contained 768 mg/kg total chlorine. Extraction of these ten samples with water typically demonstrated that a significant fraction, but not all, of the total chlorine appeared to be present as inorganic chloride. The unaccounted for chlorine may reflect the precision of the analytical methods, semivolatile chlorinated organic compounds, unanalyzed volatile chlorinated organic compounds or inorganic chlorides that were not extracted from the oil.

Three of the previously discussed waste oil samples were also analyzed for halogens. Total bromine was below 600 mg/kg in all samples. Two samples contained fluorine; 96 and 182 mg/kg. Total chlorine concentrations were in the 1,300 to 13,000 mg/kg range. Extractable inorganic chloride represented 5 to 25 percent of the total chlorine in these samples.

SECTION 9

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APPENDIX A

DISCUSSION OF POTENTIAL OIL PHASE ANALYSIS AND MASS BALANCE CONSIDERATIONS

Analysis of the oil phase (see Figure A-1), although originally planned was not included in the revised QA plan and not conducted. The results might have been interesting but probably not very significant and the analyses would have required a reduction in the already limited number of samples. If there were no volatile chlorinated organics in the sample or if no volatile chlorinated organics were lost in the extraction process, it would have been possible to calculate a mass balance for Cl. However, the validity and usefulness of this calculation is questionable as discussed in the hypothetical cases presented below.

The first case in Figure A-2 represents the results that might be expected if the oil phase is not analyzed. The data show that organic chlorinated compounds were either not present or not extracted in significant quantities, relative to inorganic chloride, by the water. Also the data show that a high percentage of the total chlorine in the oil was inorganic chloride.

The second example, in Figure A-2, which includes analysis of the oil phase leads to the same conclusion as the first case. The fact that the total Cl in the two phases is the same as the total in the oil is interesting but does not prove that the data are either precise or accurate. Precision is demonstrated by replicate analyses and accuracy is demonstrated by analysis of known samples. If the precision is ± 10 percent, then the 95 percent confidence interval for each of the single results is about ± 20 percent. Unless we analyze each sample 3 to 10 times in order to obtain a smaller confidence interval, the agreement noted in case 2 can only be interpreted as a chance event. It doesn't validate the measurements. Due to budget constraints we never considered doing multiple analyses of each sample. Further, the possible loss of volatile chlorinated organics should not be ignored.

Case 3 shows an example in which the results do not appear to agree (assuming again that we ignore the question of volatiles). The results do not lead to any new conclusions. The interpretation is similar to case 2. The results don't demonstrate any lack of precision or accuracy or other problems.

Case 4 is a hypothetical case that, if it occurred, would have indicated an analytical problem. However it is anticipated that this case would not occur and the QA procedures are a more cost effective means of detecting analytical problems.

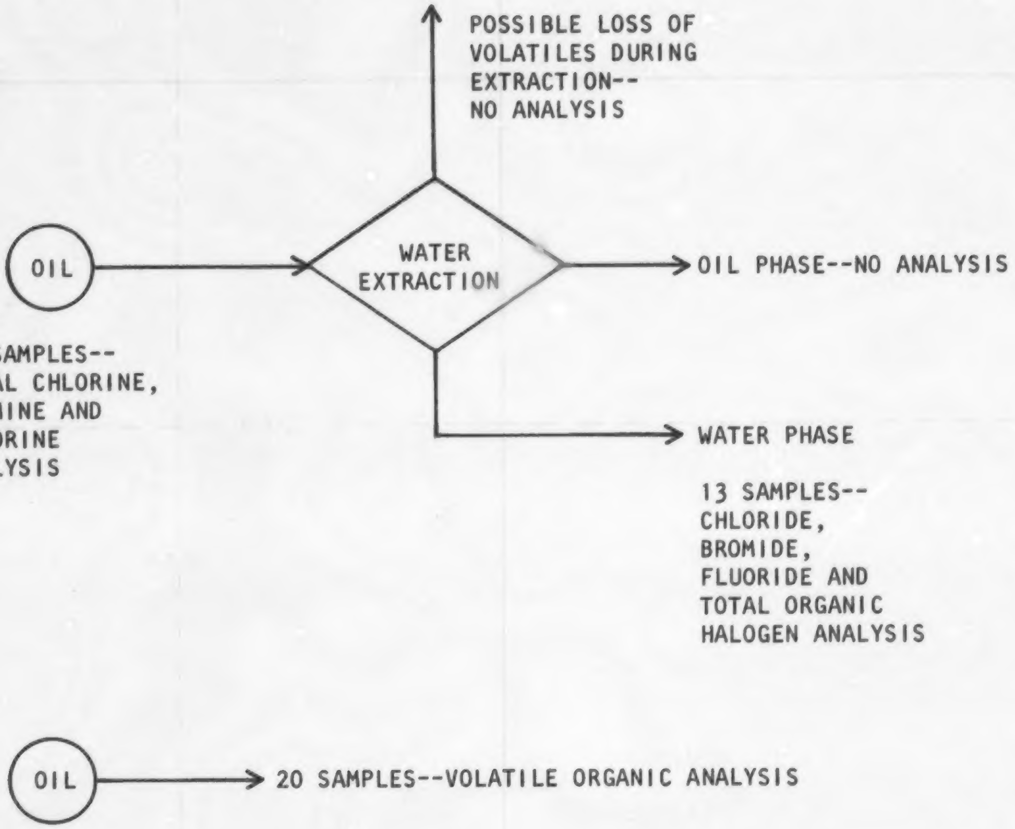
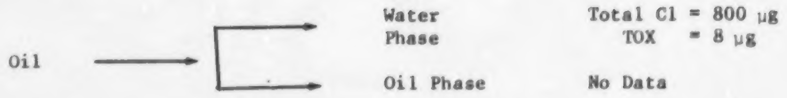

POSSIBLE LOSS OF VOLATILES DURING EXTRACTION--NO ANALYSIS
OIL
WATER EXTRACTION
OIL PHASE--NO ANALYSIS
13 SAMPLES--TOTAL CHLORINE, BROMINE AND FLUORINE ANALYSIS
WATER PHASE
13 SAMPLES--CHLORIDE, BROMIDE, FLUORIDE AND TOTAL ORGANIC HALOGEN ANALYSIS
OIL
20 SAMPLES--VOLATILE ORGANIC ANALYSIS

Figure A-1. Planned analyses of oil samples.

1. Oil Phase Not Analyzed

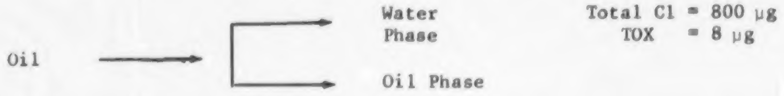

Water Phase
Total Cl = 800 μg
TOX = 8 μg
Oil
Oil Phase
No Data

Total Cl = 1000 μg

Conclusions:

a. Organic clorinated compounds were either not present or not extracted in significant quantities by the water.
b. About 80 percent of the chlorine in the oil was inorganic chloride.

2. Hypothetical Case

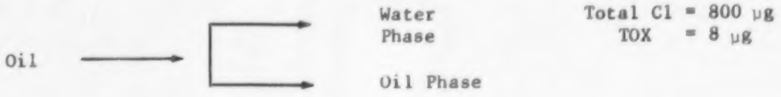

Water Phase
Total Cl = 800 μg
TOX = 8 μg
Oil
Oil Phase

Total Cl = 1000 μg   Total Cl = 200 μg

Conclusions:

a. Organic clorinated compounds were either not present or not extracted in significant quantities by the water.
b. About 80 percent of the chlorine in the oil was inorganic chloride.

3. Hypothetical Case

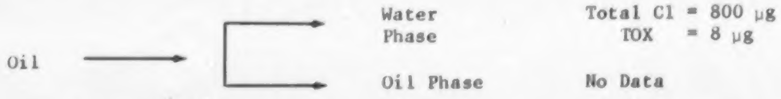

Water Phase
Total Cl = 800 μg
TOX = 8 μg
Oil
Oil Phase

Total Cl = 1000 μg   Total Cl = 400 μg

Conclusions:

a. Organic clorinated compounds were either not present or not extracted in significant quantities by the water.
b. About 80 percent of the chlorine in the oil was inorganic chloride.

4. Hypothetical Case


Water Phase
Total Cl = 800 μg
TOX = 8 μg
Oil
Oil Phase
No Data

Total Cl = 1000 μg   Total Cl = 800 μg

Conclusions:

a. Possible analytical problem.

Figure A-2. Comparison of hypothetical results for analysis of oil phase samples.

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APPENDIX B

STANDARD OPERATING PROCEDURES

The following standard operating procedures may mention products (instrumentation, chemicals, resins, etc.) by trade or brand name. This reflects only the currently used materials at GCA/Technology Division and does not constitute a value judgment on the part of GCA. Equivalent products may exist.

TOTAL HALOGENS IN PETROLEUM PRODUCTS

SCOPE AND APPLICATON

This method covers the determination of total halogens in lubricating oils and greases, including new and used lubricating oils and greases containing additives, and in additive concentrates.

SUMMARY OF METHOD

The sample is oxidized by combustion in a bomb containing oxygen under pressure. The halogen compounds thus liberated are absorbed in a sodium carbonate solution and the amount of total halogen present is determined by Ion Chromatography.

SAMPLE COLLECTION AND PRESERVATION

Limit headspace of sample containers to preclude volatilization.

INTERFERENCES

No known interferences at this time.

REAGENTS

1. Oxygen--free of combustible material and halogen compounds, available at a pressure of 40 atmospheres.

2. Sodium Carbonate Solution--Dissolve 50 g of anhydrous Na_2CO_3 in deionized water and dilute to one liter.

3. 1000 µg/ml Bromide Standard--Dissolve 1.2877g NaBr in deionized water and dilute to 1 liter.

4. 1000 µg/ml Chloride Standard--Dissolve 1.6484g NaCl in deionized water and dilute to 1 liter.

5. 1000 µg/ml Fluoride Standard--Dissolve 2.2100g NaF in deionized water and dilute to 1 liter.

6. Working Standard Solutions--Usually the following standards are prepared using deionized water for dilutions; 10 µg/ml Br^-; 1 µg/ml Cl^-; 1 µg/ml F^-; 20 µg/ml Br^-; 5 µg/ml Cl^-; 5 µg/ml F^-; 40 µg/ml Br^-; 10 µg/ml Cl^-; 10 µg/ml F^-; 50 µg/ml Br^-; 20 µg/ml Cl^-; 20 µg/ml Cl^-.

7. Air--Compressed.

8. Standard Eluent (0.003 M $NaHCO_3$: 0.0024 M Na_2CO_3)--Prepare by dissolving 1.0080 g $NaHCO_3$ and 1.0176 g Na_2CO_3 in deionized water and dilute to 4 liters.

9. Regeneration Solution (1N H_2SO_4)--Dilute 111 ml concentrated sulfuric acid to 4 liters with deionized water.

APPARATUS

1. Parr Bomb
2. Stainless steel sample cup
3. Stainless steel firing wire
4. Nylon or white cotton sewing thread
5. Ignition circuit, capable of supplying sufficient current to ignite the nylon or cotton thread without melting the wire.
6. Beakers--600 ml pyrex
7. Speedy-vaps to fit 600 ml beakers
8. Volumetric flasks--100 ml
9. Hot plates
10. Dionex Ion Chromatograph
11. Plastic syringe, 5 ml capacity
12. Millipore syringe filter unit, 0.22 µm
13. Recorder

QUALITY CONTROL REQUIREMENTS

1. Spiked samples and a reagent blank should be analyzed with each group of samples.

PROCEDURE

1. Preparation of bomb and sample: Cut a piece of firing wire approximately 100 mm in length. Coil the middle section (approximately 20 mm) and attach the free ends to the terminals. Arrange the coil so that it will be above and to one side of the sample cup. Insert a nylon or cotton thread into the coil, of such length that one end extends into the sample cup. Place 10 ml Na_2CO_3 solution in the bomb and by means of a rubber policeman wet the interior surface of the bomb, including the head, as thoroughly as possible. Weigh 0.8 g to 1.0 g sample into the sample cup.

2. Addition of oxygen: Place the sample cup in position and arrange the thread so that one end dips into the sample. Assemble the bomb and tighten the cover securely. Admit oxygen slowly (to avoid blowing the oil from the cup) until pressure is reached as indicated in the table below:

Bomb Capacity (ml)	Min. Gage Pressure atm.	Max. Gage Pressure atm.
300-350	38	40
350-400	35	37
400-450	30	32
450-500	27	29

3. Combustion: Immerse the bomb in a cold water bath. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Remove the bomb from the bath after immersion of at least 10 min. Release the pressure at a slow uniform rate such that the operation requires not less than one minute. Open the bomb and examine the contents. If traces of unburned oil or sooty deposits are found, discard the determination.

4. Collection of chloride sample: Using deionized water, rinse the interior of the bomb, the sample cup, and the inner surface of the bomb cover into a 600 ml beaker. Scrub the interior of the bomb and the inner surface of the bomb cover with a rubber policeman. Wash the base of the terminals into the beaker. Cover the beaker with a speedy vap and gently reduce volume to 75 ml or less. Remove from the hot plate and cool to room temperature. Transfer the contents of the beaker into a 100 ml volumetric flask. Rinse the beaker several times, transferring rinses to the volumetric flask. Dilute to volume.

5. Cleaning procedure for bomb and sample cup: Any residual fuse wire is removed from the bomb, including any wire fused to the bomb interior. The interior surfaces of the bomb and cover are scrubbed with a nylon brush using hot alconox solution. The bomb and cover are then copiously rinsed with deionized water. The stainless steel sample cups is sanded with 400 grit emery paper followed by scrubbing with hot alconox solution. The sample cup is then copiously rinsed with deionized water and air dried.

IC ANALYSIS

1. Set up the instrument according to the operator's manual.

2. Inject appropriate standards and record the peak heights.

3. Inject the samples and record the peak heights. Make the necessary dilutions or adjustment of the μMHO scale on the instrument to bring the sample into the linear range.

4. Calculate the linear regression data for the standards, enter the peak height value for each sample and record the calculated ppm value.

5. Calculate mg/kg halide--using the following equation:

$$\text{mg/kg Halide} = \frac{(\text{Sample } \mu\text{g/ml [from curve]} - \text{blank } \mu\text{g/ml [curve]}) \times \text{Dilution} \times \text{Sample volume (ml)}}{\text{Sample weight (g)}}$$

REFERENCE

1. Standard Test Method for Chlorine in New and Used Petroleum Products (Bomb Method) ANSI/ASTM D 808-63.

INORGANIC HALIDES IN PETROLEUM PRODUCTS

SCOPE AND APPLICATON

This method covers the semi-quantitative determination of inorganic halides in petroleum products.

SUMMARY OF METHOD

The sample is dissolved in an appropriate solvent and hot aqueous extracted. The extract is subsequently analyzed for inorganic halides by Ion Chromatography.

SAMPLE COLLECTION AND PRESERVATION

Limit headspace to preclude volatilization.

INTERFERENCES

Coeluting ions may interfere.

REAGENTS

1. n-Heptane.
2. Methyl isobutyl ketone (MIBK).
3. 1000 μg/ml Bromide Standard--Dissolve 1.2877g NaBr in deionized water and dilute to 1 liter.
4. 1000 μg/ml Chloride Standard--Dissolve 1.6484g NaCl in deionized water and dilute to 1 liter.
5. 1000 μg/ml Fluoride Standard--Dissolve 2.2100g NaF in deionized water and dilute to 1 liter.
6. Working Standard Solutions--Usually the following standards are prepared using deionized water for dilutions: 10 μg/ml Br, 1 μg/ml Cl; 1 μg/ml F; 20 μg/ml Br; 5 μg/ml Cl; 5 μg/ml F; 40 μg/ml Br; 10 μg/ml Cl; 10 μg/ml F; 50 μg/ml Br; 20 μg/ml Cl; 20 μg/ml F.
7. Air--Compressed.
8. Standard Eluent (0.003 $\underline{M}$ $NaHCO_3$: 0.0024 $\underline{M}$ Na_2CO_3)--Prepare by dissolving 1.0080 g $NaHCO_3$ and 1.0176 g Na_2CO_3 in deionized water and dilute to 4 liters.
9. Regeneration Solution (1N H_2SO_4)--Dilute 111 ml concentrated sulfuric acid to 4 liters with deionized water.

APPARATUS

1. Damon IEC EXD Centrifuge
2. Centrifuge bottles--200 ml capacity
3. Volumetric pipets--20, 25 ml capacity
4. Nalgene bottles
5. Dionex Ion Chromatograph
6. Plastic syringe, 5 ml capacity
7. Millipore syringe filter unit, 0.22 μm
8. Recorder
9. Hot plate
10. Thermometer
11. Beaker--600 ml capacity

QUALITY CONTROL REQUIREMENTS

1. Reagent blank and spiked extracts should be analyzed with each group of samples.

PROCEDURE

1. Preparation of sample for extraction: Test aliquots of oil samples for solubility in n-heptane and MIBK. Proceed utilizing the solvent most miscible with sample. Weight approximately 10g sample into tared centrifuge bottle. Pipet 20 ml solvent into the bottle. Shake vigorously, venting as necessary until sample and solvent are homogeneous.

2. Extraction: Pipet 25 ml 95°C deionized water into the centrifuge bottle. Cap and shake vigorously for 5 min., venting when necessary. Pipet second 25 ml aliquot 95°C deionized water into bottle, cap, and shake vigorously for 5 min.

3. Phase separation and sample collection: Centrifuge the bottle from the centrifuge. If phase separation is incomplete, return for longer centrifugation. Allow the fractions to separate. Withdraw the aqueous phase by pipet to a nalgene bottle. Repeat steps 3 and 4 delivering the second extract to the first.

IC ANALYSIS

1. Set up the instrument according to the operator's manual.
2. Inject appropriate standards and record the peak heights.
3. Inject the samples and record the peak heights. Make the necessary dilutions or adjustment of the μMHO scale on the instrument to bring the sample into the linear range.
4. Calculate the linear regression data for the standards, enter the peak height value for each sample and record the calculated ppm value.
5. Calculate mg/kg Cl using the following equation:

$$\text{mg/kg Cl} = \frac{\begin{gathered}(\text{Sample } \mu\text{g/ml [from curve]} - \text{blank } \mu\text{g/ml [curve]}) \times \\ \text{Dilution} \times \text{Extract volume (ml)}\end{gathered}}{\text{Sample weight (g)}}$$

REFERENCE

1. Standard Test Method for Inorganic Chlorides and Sulfates in Insulating Oils ANSI/ASTM D 878-65.

AUTOMATED CHLORIDE ANALYSIS BY FERRICYANIDE

SCOPE AND APPLICATION

This method covers the determination of chloride in drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 1 to 200 μg/ml.

SUMMARY OF METHOD

Thiocyanate ion is liberated from mercuric thiocyanate through the sequestration of mercury by chloride ion to form un-ionized mercuric chloride. The liberated thiocyanate in the presence of ferric ion forms highly colored ferric thiocyanate in concentration proportional to the chloride concentration.

SAMPLE COLLECTION AND PRESERVATION

No special requirements.

INTERFERENCES

No significant interferences.

REAGENTS

1. Mercuric Thiocyanate Solution--Dissolve 4.17g Hg(SCN)2 in 500 ml methanol. Dilute to 1 liter with methanol, mix and filter through filter paper.
2. Ferric Nitrate Solution, 20.2 percent--Dissolve 202g of $Fe(NO_3)_3 \cdot 6H_2O$ in 500 ml deionized water. Add 31.5 ml conc nitric acid, mix and dilute to 1 liter with deionized water.
3. Color Reagent--Add 150 ml mercuric thiocyanate solution (1) to 150 ml ferric nitrate solution, (2) mix, and dilute to 1 liter with deionized water.
4. 1000 μg/l Chloride Standard--Dissolve 1.6484g predried (140° C) NaCl in deionized water and dilute to 1 liter.
5. Working Standard Solutions--Usually the following standards are prepared using deionized water for dilutions: 1 μg/ml, 5 μg/ml, 10 μg/ml, and 15 μg/ml.

APPARATUS

1. Technicon Auto Analyzer II Sampler, Pump, and Colorimeter.
2. 480 nm filters, pair.
3. Recorder.

4. Volumetric flasks--appropriate for required dilutions.

5. Pipets--appropriate for dilutions.

6. Filter papers.

QUALITY CONTROL REQUIREMENTS

1. Spiked samples, method blank where appropriate, and LCS should be analyzed with each group of samples.

PROCEDURE

1. Set up Technicon according to Figure B-1. Twenty-five or 50 mm flow cells may be substituted where lower sensitivity is required.

2. Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding deionized water through the sample line until the system is stable.

3. Place working standards in sampler in order of decreasing concentrations. Complete filling tray with quality control and program samples.

4. Start the sampler after establishment of stable baseline. Analyze the program samples after verification of the correct LCS value.

5. Calculate the liner regression data for the standards, enter the percent scale value for each sample and record the calculated μg/ml value.

6. When applicable, subtract the method blank value (μg/ml) from the sample value (μg/ml) to arrive at the correct sample concentration.

7. Calculate μg/ml Cl--using the following equation:

   μg/ml Cl = Sample μg/ml (blank corrected where appropriate) x Dilution

8. Calculate mg/kg Cl--using the following equation:

$$\text{mg/kg Cl} = \frac{\text{Sample } \mu\text{g/ml (blank corrected where appropriate) x Dilution x Sample volume (ml)}}{\text{Sample weight (g)}}$$

REFERENCE

1. Methods for Chemical Analysis of Water and Wastes, Method 325.2, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. Revised March 1983.

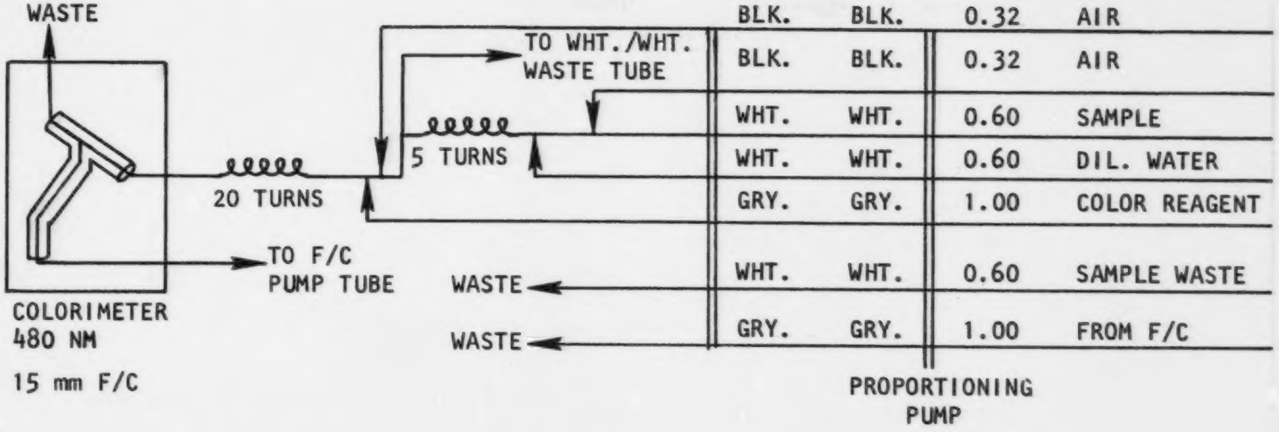
WASTE
COLORIMETER
480 NM
15 mm F/C
20 TURNS
TO F/C
PUMP TUBE
5 TURNS
TO WHT./WHT.
WASTE TUBE
WASTE
WASTE
BLK. BLK. 0.32 AIR
BLK. BLK. 0.32 AIR
WHT. WHT. 0.60 SAMPLE
WHT. WHT. 0.60 DIL. WATER
GRY. GRY. 1.00 COLOR REAGENT
WHT. WHT. 0.60 SAMPLE WASTE
GRY. GRY. 1.00 FROM F/C
PROPORTIONING
PUMP

Figure B-1. Chloride manifold, AutoAnalyzer II.

TOTAL ORGANIC HALIDES ANALYSIS

SCOPE AND APPLICATON

This method covers the determination of total organic halides in waters and aqueous extracts of other sample matrices.

SUMMARY OF METHOD

The sample is passed over granulated activated carbon (GAC) to adsorb the halogen constituents. Subsequently the columns are rinsed with nitrate solution to remove the inorganic halides. The GAC is then pyrolyzed to convert the organohalides to a titratable species that can be measured by a microcoulometric detector as chloride.

SAMPLE COLLECTION AND PRESERVATION

Headspace should be limited to minimize loss of volatiles. Residual chlorine should be reduced by the addition of 1 ml of 0.1 M sodium sulfite.

INTERFERENCES

All gases should be high purity. All glassware should be cleaned and baked out to reduce the introduction of contamination.

REAGENTS

1. Oxygen--zero grade or equivalent purity.

2. Carbon Dioxide--zero grade or equivalent purity.

3. Nitrogen--prepurified grade.

4. 5000 μg/ml Nitrate Solution--Dissolve 8.2g of KNO_3 in deionized water and dilute to 1 liter.

5. Nitric Acid-Instra or Ultrex grade.

6. 1000 μg/ml Chloride Standard Solution--Dissolve 1.6484g NaCl in deionized water and dilute to 1 liter.

7. 500 ng/μl 2,4,6-Trichlorophenol Standard Solution--Dissolve 92.8g 2,4,6-Trichlorophenol in methanol and dilute to 100 ml with methanol.

8. Acetic Acid--70%.

APPARATUS

1. Dohrmann DX-20, AD-2 Adsorption Module, MC-1 Analyzer Module

QUALITY CONTROL REQUIREMENTS

1. Spiked samples, reagent blank, and extraction blank where applicable should be run with each set of samples.

PROCEDURE

1. Calibration: Set up instrument according to manufacturer's instructions.

2. Adsorption: Two GAC solumns are prepared for each sample analysis by filling glass columns with 40 mg 10/40 mesh GAC and plugging the ends with cerafelt. The sample reservoir is filled with approximately 120 ml. The sample is then passed over the GAC by charging the reservoir with nitrogen at a pressure of 20 psi. The adsorption is halted at a known volume sample collected, usually 100 ml.

3. Speciation: The GAC columns are subsequently rinsed with 5000 μg/ml nitrate solution at an applied pressure of 5 psi to remove inorganic halides.

4. Pyrolysis: The GAC are removed from the individual glass columns and analyzed separately. The first GAC and plugs are delivered to the quartz boat and carried through the two step pyrolysis. The sample is advanced to the vaporization mode for 2 min at 250°C in a CO_2 rich atmosphere. The sample is then carried through an 800°C pyrolysis in a O_2 rich environment for 6 min. The sample then goes through a 2 min cool down. After removal of the first GAC, the second GAC and plugs are then delivered to the quartz boat and carried through the analytical sequence.

5. Detection: The titratable halides are swept into the microcoulometric titration cell for analysis. The concentraton is read out digitally as total μg chloride.

6. Calculate μg/l TOX using the following equation:

$$\text{TOX } (\mu\text{g Cl/l}) = \frac{\text{Sample (GAC1 + GAC2) - Blank (GAC1 + GAC2) x Dilution}}{\text{Sample volume (l)}}$$

7. Calculate mg/kg TOX for oil extracts using the following equation:

$$\text{TOX (Cl/kg)} = \frac{\begin{array}{c}\text{Sample (GAC1+GAC2)-Extract Blank (GAC1+GAC2)/analysis volume (ml)}\\ \text{x Extraction volume (ml)}\end{array}}{\text{Sample weight (g)}}$$

REFERENCE

1. Total Organic Halide, Interim Method. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio. November 1980.

2. DX-20 Total Organic Halide Analyzer System. Dohrmann Division Envirotech Corp. Santa Clara, CA.

VOLATILE ORGANICS: TETRAGLYME EXTRACTION WITH MODIFIED METHOD 624 ANALYSIS

SCOPE AND APPLICATION

This method is designed to prepare a variety of nonaqueous samples for analysis for volatile organic compounds. It is applicable to oils, sludges, and solid wastes. It allows the detection and quantitation of organic compounds amenable to analysis by the purge and trap method as outlined in Method 624.

SUMMARY OF METHOD

A 1 gram portion of sample is extracted with 20 ml of tetraglyme. After phase equilibration, the tetraglyme layer is withdrawn, placed in a screw-cap vial with a minimum of headspace, and stored at 4°C for subsequent analysis. At the time of analysis, an aliquot of the extract is spiked into 25 ml of deionized water and Method 624 protocols are followed for the determination of volatile organics.

SAMPLE COLLECTION AND PRESERVATION

Samples collected for volatile organics analysis should be placed in 40 ml glass vials equipped with a septum-lined screw cap (as in 624).

1. Fill the sample vial as completely as possible. Nonfluid samples should be packed into the vial with a minimum of headspace; fluid samples should be collected so no air bubbles remain in the vial.

2. Seal the vial.

3. Collect a duplicate sample.

4. Store the sample at 4°C until the time of extraction.

INTERFERENCES

1. See Method 624.

2. Daily analysis of method blanks--Analyze a sample of deionized water taken from the Inorganic Wet lab and spiked with 100 μl of tetraglyme from the same batch as that used for sample extraction.

3. After each analysis, rinse the purge tube with deionized water. Bake the trap for a minimum of 20 min. to ensure adequate desorption of high molecular weight purgeables. Nonaqueous samples typically contain more high-molecular weight material than do water samples, and the possibility of system contamination must be recognized.

4. Sample analysis time should be a minimum of 40 minutes to allow elution of higher boiling purgeables. Each chromatogram should be checked for possible chromatographic carryover; should this be suspected, the trap and oven should be baked out for 30 minutes before sample analysis continues.

REAGENTS

1. See Method 624.

2. Tetraglyme (tetraethylene glycol dimethylether)--cleaned by placing in a rotary evaporator under aspirator suction for a minimum of 2 hours. The flask is immersed in a water bath at 90 to 100°C during this period. Tetraglyme cleaned in this fashion should be analyzed prior to use for extraction. A 100 µl aliquot spiked into 25 ml of deionized water should not interfere with detection of the internal standards used in Method 624 or cause baseline elevation greater than 30 percent the peak height of the highest internal standard used for analysis.

3. Calibration standards--standards used for Method 624 analysis are spiked with 100 µl tetraglyme prior to calibration curve analyses. Alternatively, stock solutions of the analytes may be prepared in tetraglyme either from pure reference materials or from Supelco solutions. Aliquots of the tetraglyme stock are spiked into water to prepare standards at the working levels.

PROCEDURE

Tetraglyme Extraction

1. Weigh 1 gram portion of sample into a precleaned 40 ml glass screw cap vial.

2. Cover the sample immediately with 20 ml of tetraglyme measured with a delivery pipette.

3. Replace the vial cap and shake the vial until the layers mix or emulsify (no longer than 1 minute). If the sample is solid or highly viscous, sonication should be performed with a sonicator probe for 30 seconds at a setting of 5 and a 25 percent pulsed duty cycle.

4. Allow the tetraglyme/sample mixture to equilibrate until the layers are clearly separated. The appropriate time will vary with sample type; oil samples should be stored at 4°C overnight in contact with the tetraglyme while extracts from solids will require less time. Some samples may completely mix with the tetraglyme to form a solution.

5. Withdraw the tetraglyme layer and place in a precleaned screw cap glass vial. Allow a minimum of headspace. Store at 4°C.

Method 624 Analysis

1. The volume of tetraglyme extract appropriate for Method 624 analysis within the established calibration curve will vary with the level of volatile content of the original sample. If this is known to an approximation, the volume of tetraglyme extract to be used for analysis may be calculated by the following equation. This equation is based upon the assumption that tetraglyme added to 25 ml water will give most accurate quantitation if the resultant solution is in the middle range of the calibration curve, or about 100 μg/l, for organic volatiles.

   Volume of tetraglyme to use (ml) =

$$\frac{100\ \mu\text{g/l} \times 0.025\ \text{liter} \times 20\ \text{ml tetraglyme extract}}{\text{Sample wt (g) extracted} \times \text{sample contaminant levels } (\mu\text{g/g})}$$

2. For samples of unknown content, a nominal 10 μl aliquot is measured with a 25 μl syringe and spiked into 25 ml of deionized water.

3. Analysis is conducted by purge and trap protocol as outlined in Method 624.

4. The total ion chromatogram is reviewed after analysis to determine whether maximum detection for the sample has been achieved without instrument saturation. This is done by monitoring the abundance of the base peak for major organic volatile components. The mass spectrometer is saturated when the count for the base peak of a compound exceeds 32767 for a single scan. If the maximum counts for the base peaks of the compounds detected as major components are less than 3000, detection limits may be reduced by an order of magnitude or greater. Reanalysis using 100 μl or greater portions of the tetraglyme extract may be conducted without instrument saturation occurring.

   If instrument saturation occurs during the analysis of the 10 μl tetraglyme aliquot, base peak counts for a single scan will exceed 32767. If this is noted, reanalysis should be conducted on a 1 μl aliquot of the extract.

Sample Quantitation

1. Determine the level of organic components in the water solution using the established calibration curve.

2. Calculate the level of sample content by the following equation:

Sample concentration (μg/g) =

$$\frac{\text{Water conc. } (\mu\text{g/l}) \times 0.025\ \text{liter} \times 20\ \text{ml tetraglyme}}{\text{Vol. of tetraglyme extract spiked into water} \times \text{wt of sample extracted (g)}}$$

3. Determine detection limits for the original sample by the following equation:

$$\text{Detection limit for oil sample } (\mu g/g) = \frac{\text{Method detection limit } (\mu g)}{\text{Volume of tetraglyme extract analyzed (ml)}} \times \frac{\text{Volume of tetraglyme used for extraction (ml)}}{\text{Weight of oil sample extracted (g)}}$$

VOLATILE ORGANICS

(FEDERAL REGISTER METHOD 624 - CONSULT F.R. FOR DETAILS)

1.0 SCOPE AND APPLICATION

This method is designed to detect and quantify volatile organic compounds which are amenable to the purge and trap method; the compounds routinely determined by this procedure are shown in Table B-1.This method has been approved for NPDES monitoring.

2.0 SUMMARY OF METHOD

A 25-ml sample is purged with a stream of helium. The volatile organics present in the sample are transferred to the vapor phase and trapped on a sorbent column. After purging is completed, the sorbent column is heated and backflushed with helium to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components which are detected by a mass spectrometer.

3.0 SAMPLE COLLECTION AND PRESERVATION

Grab samples are collected in 40-ml glass vials equipped with a septum and screw cap. Prior to use, the vials, caps and septa must be soap- and water-washed, rinsed with deionized water and dried at 105°C for 1 hour. The following procedure is used for sample collection and storage.

3.1 Fill the sample vial completely, do not allow any air bubbles to pass through the sample.

3.2 Seal the vial; check that no air bubbles have been trapped in the sample.

3.3 Collect a duplicate sample.

3.4 Store sample at 4°C until the time of analysis; analysis must be performed within 14 days of sample collection.

4.0 INTERFERENCES

A variety of interfering substances may be present in more complex samples such as industrial effluents. The most common problem associated with this analysis is contamination; the following steps should be taken to detect contamination introduced in sample handling or analysis.

4.1 Analysis of field biased blanks--Deionized water carried through the sampling, storage and analysis procedures.

4.2 Daily analysis of method blanks--Analyze a sample of deionized water at the start of each analysis session, this detects contamination introduced by the purge gas or the plumbing ahead of the trap.

TABLE B-1. REPORTED COMPOUNDS AND THEIR CHARACTERISTIC IONS

Compound	Primary Ion
chloromethane	50
dichlorodifluoromethane	85
bromomethane	94
vinyl chloride	62
chloroethane	64
methylene chloride	84
trichlorofluoromethane	101
1,1-dichloroethylene	96
1,1-dichloroethane	63
trans-1,2-dichloroethylene	96
chloroform	83
1,2-dichloroethane	98
1,1,1-trichloroethane	97
carbon tetrachloride	117
bromodichloromethane	83
bis-chloromethyl ether	79
1,2-dichloropropane	63
trans-1,3-dichloropropene	75
trichloroethylene	130
dibromochloromethane	129
cis-1,3-dichloropropene	75
1,1,2-trichloroethane	83
benzene	78
2-chloroethylvinyl ether	106
bromoform	173
1,1,2,2-tetrachloroethene	166
1,1,2,2-tetrachloroethane	83
toluene	91
chlorobenzene	112
ethylbenzene	91
acrolein	56
acrylonitrile	53

4.3 After analysis of a high level sample, a blank of deionized water should be analyzed to ensure that contamination of subsequent samples by carry-over does not occur.

5.0 REAGENTS

5.1 Organic-free deionized water--Water from the Continental deionized water system should be used. To avoid possible contamination by methylene chloride, obtain the water from the tap in the Inorganic Wet Lab.

5.2 Sorbent Trap Materials

a. 2,6-Diphenylene oxide polymer - 60/80 mesh Tenax, chromatographic grade.

b. Methyl silicone packing - 3 percent OV-1 on 60/80 mesh Chromosorb W.

c. Silica gel, Davison Chemical, 35/60 mesh, grade 15.

5.3 Calibration Standards

5.3.1 Stock solutions* - 2 mg/ml: With the exception of the gases, the stock standard solutions may be either purchased from Supelco or prepared from the pure compound. Stock solutions for the gases (bromomethane, chloroethane, chloromethane and vinyl chloride) are always purchased. If stock solutions are prepared from the pure compound the following procedure is used:

a. Place 9.8 ml of methanol in a 10 ml ground glass stoppered volumetric flask.

b. Allow flask to stand unstoppered for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

c. Using a 100 μl syringe, add 2 to 3 drops of the standard material to the flask. Be certain that the drops fall directly into the alcohol without contacting the neck of the flask. Reweigh the flask.

4. Store stock standards at 4°C; prepare fresh standards every 2 weeks.

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*For this project, stock solutions of standards were purchased from Supelco. These were used to prepare dilutions at the concentrations noted in the Standard Operating Procedures. Prior to analyses, tetraglyme was added to the calibration solution to provide purging conditions comparable to those for sample analyses.

5.3.2 Working Standard Solutions

a. Prepare 100 ml of each of the following working standard solutions by dilution of the stock solutions: 5, 10, 50, 100, 150 µg/l.

5.4 Internal Standard Solution

5.4.1 The internal standard spiking solution is prepared by dilution of the Supelco standard which contains the three internal standards, bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane, at a concentration of 20 mg/ml. Alternately, this solution may be prepared from the stock standards.

5.4.2 Add 1 ml of the Supelco standard solution to 90 ml of deionized water in a 100 ml volumetric flask.

5.4.3 Dilute to volume and invert to mix. The concentration of this solution is 0.20 mg/ml. Each sample is spiked with 2.5 µl of this solution.

5.4.4 Prepare a fresh internal standard solution monthly.

5.5 UHP Helium--used as purge gas and GC carrier gas.

6.0 APPARATUS

6.1 Hewlett-Packard 5985 GC/MS.

6.2 Purge and Trap Device - Tekmar LSC 3.

6.3 GC Column - 1 Percent SP-1000 on Carbopack B, 6 ft x 2 mm ID column.

6.4 Syringe - glass, 25-ml hypodermic with Luer-Lok tip.

6.5 Microsyringes - 10, 25, 100 µl.

6.6 Volumetric glassware for preparation of standards.

7.0 QUALITY CONTROL REQUIREMENTS

7.1 A method blank of deionized water must be analyzed daily.

7.2 The volatiles laboratory control sample (LCS) must be analyzed daily. The reported value for each of the parameters should be entered in the instrument logbook. If the reported values for any of the components of the LCS are outside the established control limits (±2S), corrective action should be taken prior to running samples.

8.0 CALIBRATION AND TUNING

8.1 A five-point calibration curve is used, a new calibration curve is prepared every 2 weeks. Run each of the five working standard solutions as outlined in the procedures section. The information regarding response ratio versus area ratio for each standard is stored in the computer and used to calculate sample concentration.

8.2 Calculate the response factor (RF) for each compound using the following equation:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where A_s = Area of the primary characteristic ion for the compound to be measured.

A_{is} = Area of the primary characteristic ion of the internal standard.

C_{is} = Concentration of the internal standard.

C_s = Concentration of the compound to be measured.

8.3 The instrument should be tuned daily according to the following procedures:

8.3.1 Allow column oven and trap to heat to their maximum temperatures (220°C and 180°C, respectively).

8.3.2 Tune the instrument with DFTPA using the following criteria:

Mass	Ion Abundance Criteria
69	100%
131	28-35% of mass 69
219	22-28% of mass 69

The ion abundance values for mass 131 and mass 219 should differ by 4 to 8 percent.

8.3.[illegible] After allowing the column and trap to cool, analyze the Laboratory Control Sample.

9.0 PROCEDURE

9.1 Remove standards and samples from cold storage at least 1 hour prior to analysis and allow to warm to room temperature.

9.2 Adjust the helium flow rate to 40 ml/minute. Attach the trap inlet to the purging device and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 Remove the plunger from a 25-ml syringe; open the sample or standard bottle and pour the sample or standard into the syringe barrel until it overflows. Replace the syringe plunger and adjust the sample volume to 25-ml. Replace the cap on the sample bottle and return to cold storage.

9.4 Remove the Luer tip of the 25-ml syringe and add 2.5 μl of the internal standard solution; replace the Luer-Lok.

9.5 Inject the sample into the purging chamber.

9.6 Purge with helium to transfer the volatile components to the trap. Adjust helium flow rate to 40 ml/min. Set the purging device to purge and purge the sample for 10.0 ± 0.1 minutes at ambient temperature.

9.7 After 10 minutes of purging adjust the device to the desorb mode and begin GC/MS analysis and data acquisition using the following conditions:

GC Conditions

GC Column	1% SP-1000 on Carbopack B, 6 ft x 2 mm ID column.
Temperature Program	Isothermal at 60°C for 4 min, then 10°/min to 220°C and held at that temperature for 15 min.
Injector Temperature	225°C
Carrier Flow	UHP helium, 30 ml/min.

Purge and Trap Conditions

Desorption Temperature	180°C
Desorption Time	4 min
Oven Temperature	200°C

MS Conditions

Emission	300 μa
Electron Energy	70 eV
Scan Rate	133.3 amu/sec
Mass Interval	41-350 amu

10.0 QUALITATIVE AND QUANTITATIVE DETERMINATION

10.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other characteristic ions. The following criteria must be met for a qualitative identification:

10.1.1 The characteristic ions of each compound of interest must maximize in the same scan or within one scan of each other.

10.1.2 The retention time must fall within ±60 seconds of the retention time of the authentic compound.

10.1.3 The relative peak heights of the characteristic ions in the EICPs must fall within ±20 percent of the relative intensities of these ions in a reference mass spectrum. The reference mass spectrum may be that of a standard or from a reference library.

10.1.4 Table A-1 shows the compounds routinely reported and the primary ion used to quantify each.

10.1.5 Quantitative determination of each compound is done using the internal standard method. Calculate the concentration of each compound according to the following equation:

$$\text{Concentration: } \mu g/l = \frac{(A_s)(C_{is})}{(A_{is})(RF)}$$

where A_s = Area of the primary characteristic ion of the compound to be measured.

C_{is} = Concentration of the internal standard in g/l in the samples.

A_{is} = Area of the primary characteristic ion of the internal standard.

RF = Response factor of the compound being quantified.

These calculations are normally performed by the HP 5985 computer.

11.0 REFERENCE

11.1 Method 624, Federal Register, Monday, December 3, 1979, 40 CFR Part 136.

APPENDIX C

CHROMATOGRAMS AND RAW DATA

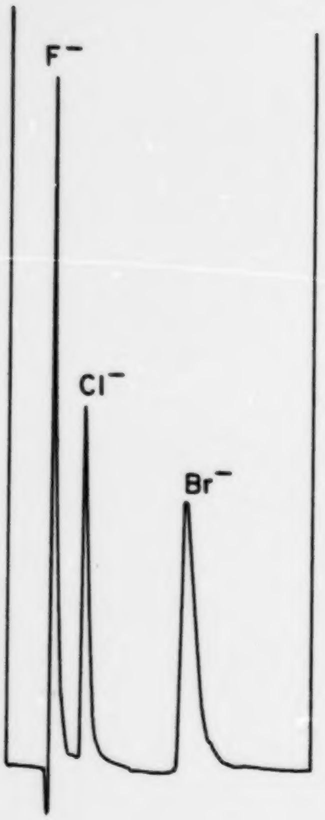

Figure C-1. Calibration standard ion chromatogram
5 µg/ml F$^-$, 5 µg/ml Cl$^-$, 20 µg/ml Br$^-$

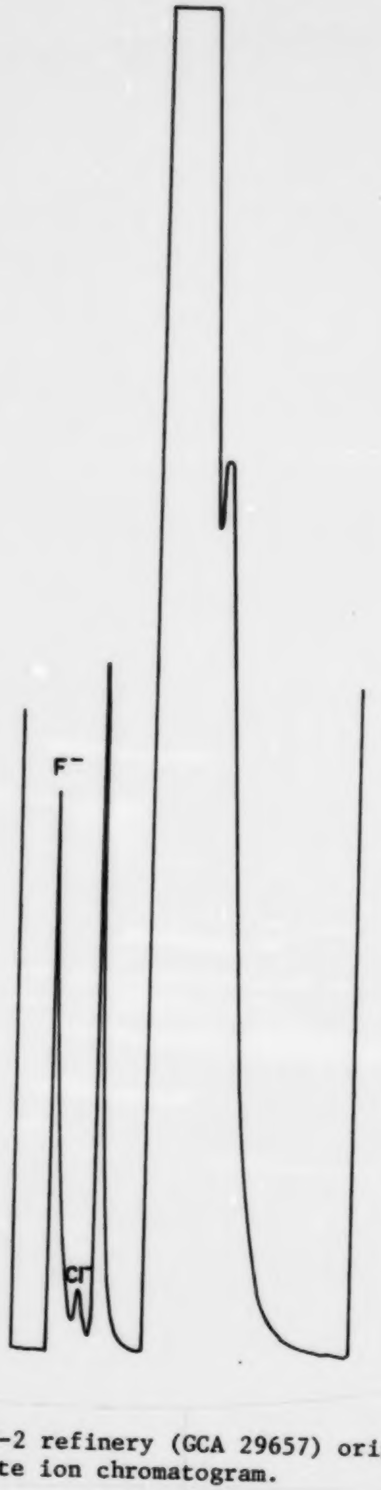

Figure C-2. 20328-NJ-2 refinery (GCA 29657) original concentration combustate ion chromatogram.

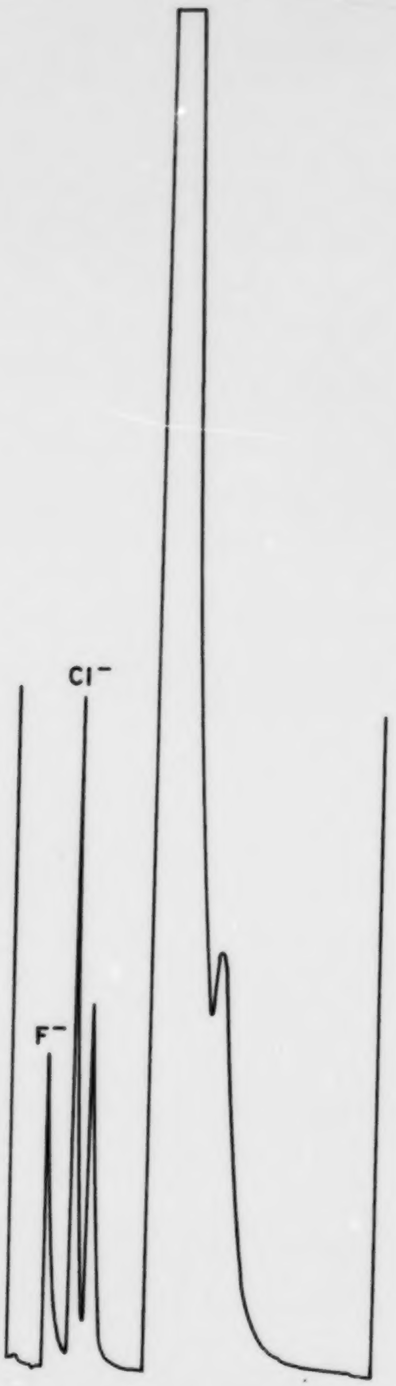

Figure C-3. 20328-NJ-2-refinery (GCA 29657) 2x dilution + 10 μg/ml Cl^- spike ion chromatogram.

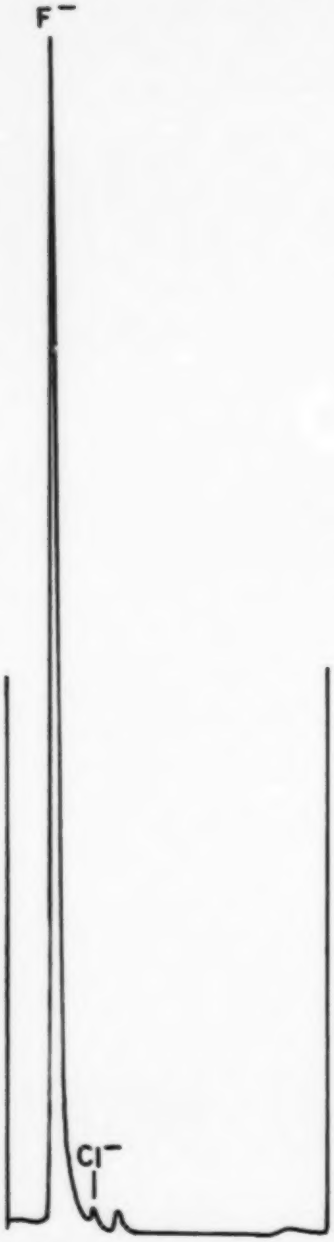

Figure C-4. Carbonate fired blank ion chromatogram.

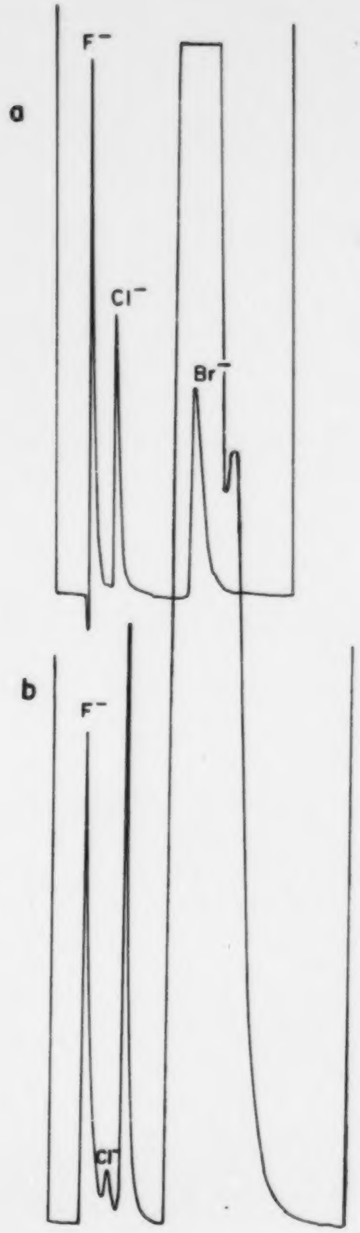

Figure C-5. a. Calibration standard ion chromatogram (5 μg/ml F$^-$, 5 μg/ml Cl$^-$, 20 μg/ml Br$^-$)
b. 20328-NJ-2-refinery (GCA 29657) original combustate ion chromatogram

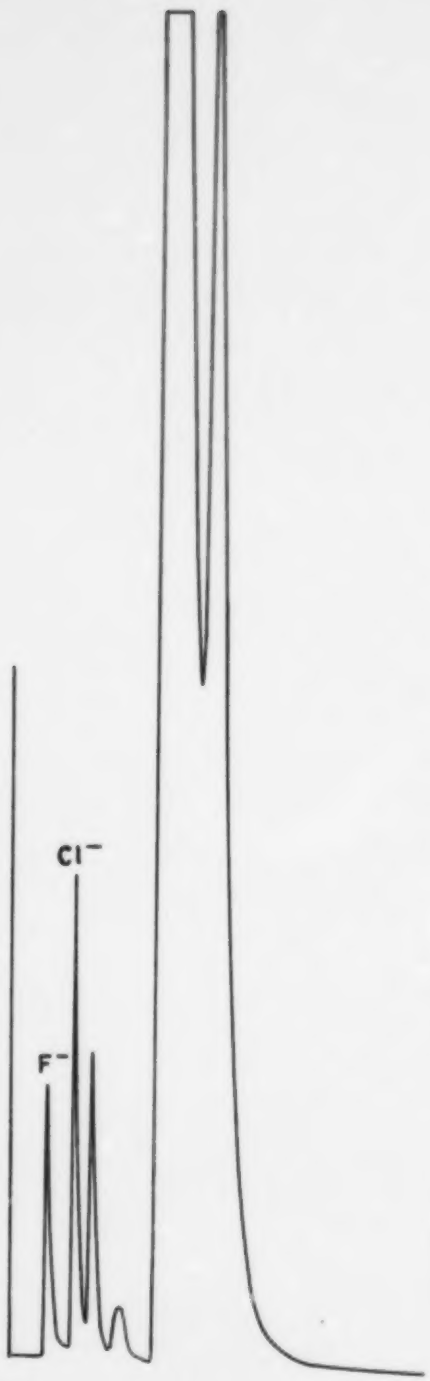

Figure C-6. WH188A-NJ-waste oil (GCA 29676) 2x dilution combustate ion chromatogram.

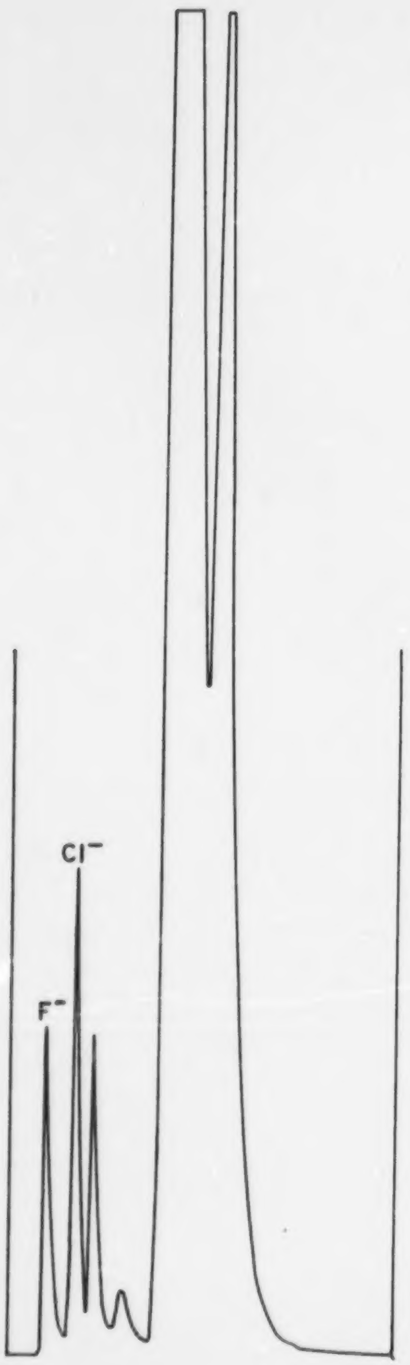

Figure C-7. WH188A-NJ-waste oil (GCA 29676) 2x dilution combustate + 10 μg/ml Br^- ion chromatogram.

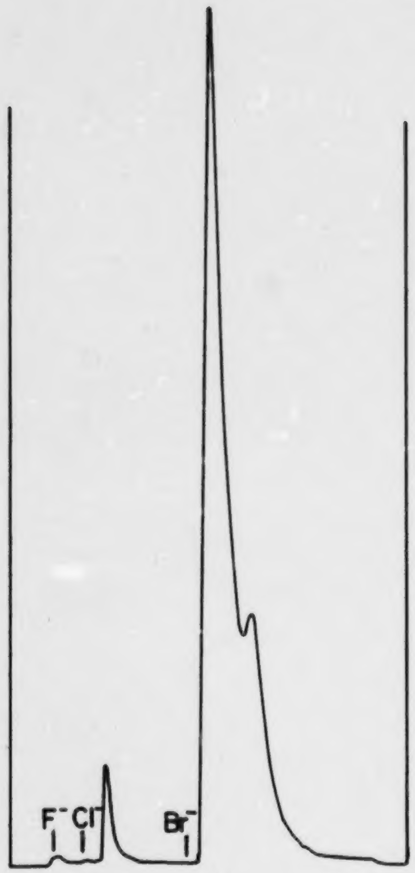

Figure C-8. 20327-NJ-6 refinery (GCA 29656) 10x dilution combustate ion chromatogram.

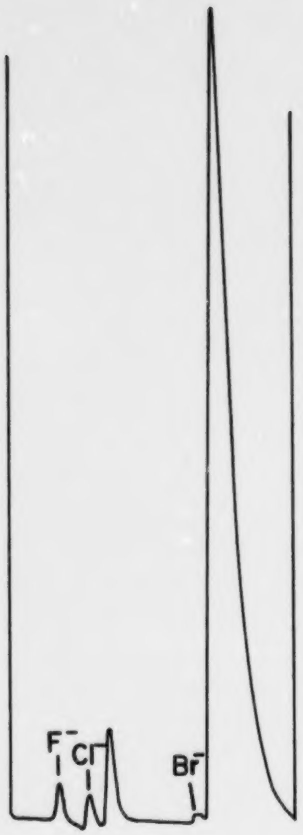

Figure C-9. Mineral oil spiked at 1035 mg/kg Br 10x dilution combustate ion chromatogram.

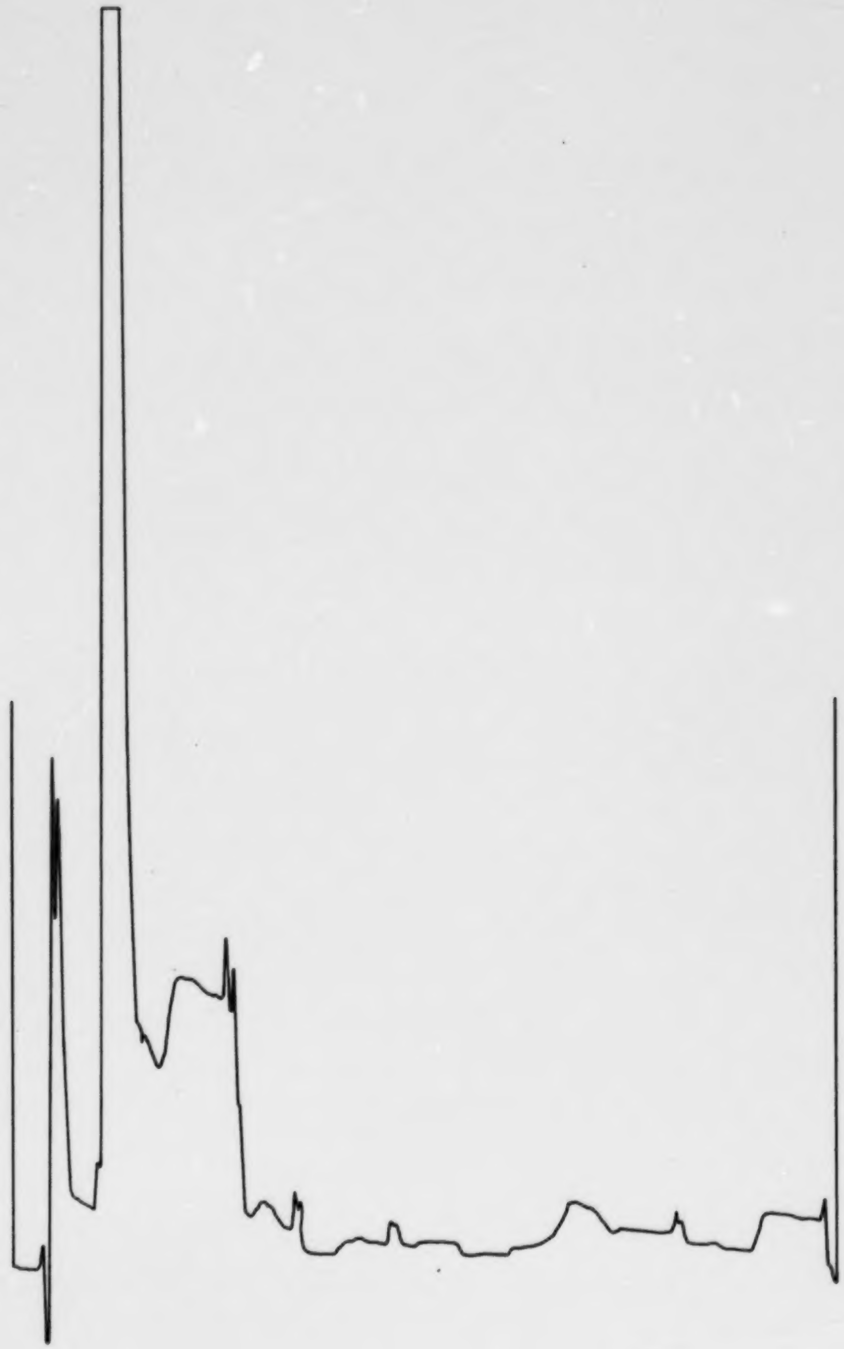

Figure C-10. (GCA 29642) aqueous extract ion chromatogram.

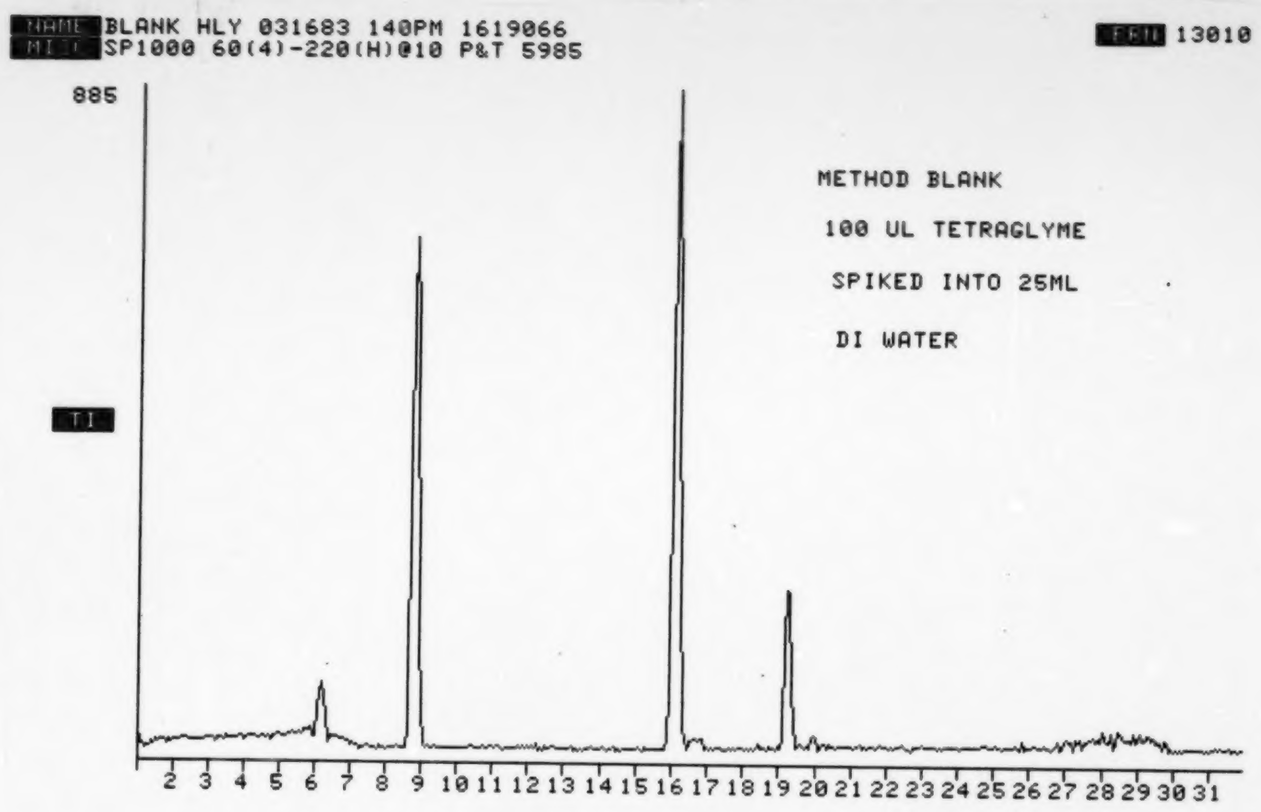

Figure C-11. Method blank.

PRIORITY POLLUTANT REPORT SHEET

VOLATILE ORGANIC COMPOUNDS

SAMPLE NUMBER	BLANK
DESCRIPTION	100 UL TETRAGLYME
DATE	031683
PROJECT #	1619066

COMPOUND	CONCENTRATION
NONE DETECTED > 0.5PPB	

```
AREA TABLE ENTRIES: FRN 13010

Entry  Time    Mass          Area       %

  1     6.2    83.7          148.    24.8
  2     8.8   127.7          595.   100.0
CALCULATE % ON ENTRY #:



AREA TABLE ENTRIES: FRN 13010

Entry  Time    Mass          Area       %

  1    16.1    76.7         1983.   100.0
CALCULATE % ON ENTRY #:


AREA TABLE ENTRIES: FRN 13010

Entry  Time    Mass          Area       %

  1    19.3    54.7          376.   100.0






  2    20.0    90.7           46.    12.1
CALCULATE % ON ENTRY #:
```

BLANK
1-619-066
3/16/83

CALIBRATION DATA: PRIORITY POLLUTANT VOLATILE ORGANIC STANDARDS ANALYZED 3/15/83 BY GC/MS

- Standards prepared in tetraglyme were spiked into organic free laboratory water to provide solutions at concentration levels of 2, 10, 50, 100 and 200 ppb. Internal standards were spiked in at a concentration of 20 ppb.

- Standards were analyzed and extracted ion areas measured for all compounds.

- The concentration ratios and corresponding area ratios were entered into computer program which establishes calibration curves.

```
CHLOROMETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?3

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                    AREA
         RATIO                        RATIO
1      ?2.5                            ?.632

2      ?5                              ?1.444

3      ?10                             ?2.9


SET*1      CC=.999619
           SLOPE=3.32193
           INTERCEPT=.323352



BROMOMETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                    AREA
         RATIO                        RATIO
1      ?.1                             ?.218

2      ?.5                             ?.976

3      ?2.5                            ?6.277

4      ?5                              ?12.86

5      ?10                             ?21.045


SET*1      CC=.998471           SET*3      CC=.991873
           SLOPE=.392966                   SLOPE=.511968
           INTERCEPT=4.16193E-02           INTERCEPT=-1.02397

SET*2      CC=.999998
           SLOPE=.378704
           INTERCEPT=.127706



VINYL CHLORIDE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                    AREA
         RATIO                        RATIO
1      ?.1                             ?.128

2      ?.5                             ?.546

3      ?2.5                            ?4.193

4      ?5                              ?8.941

5      ?10                             ?16.15
```

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```
SET*1     CC=.998043              SET*3     CC=.99742
          SLOPE=.573915                     SLOPE=.632658
          INTERCEPT=.102251                 INTERCEPT=-.342259

SET*2     CC=.999934
          SLOPE=.535566
          INTERCEPT=.224483


CHLOROETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                  AREA
         RATIO                      RATIO
1     ?.1                            ?.119

2     ?.5                            ?.404

3     ?2.5                           ?3.004

4     ?5                             ?6.191

5     ?10                            ?10.876

SET*1     CC=.997795              SET*3     CC=.996746
          SLOPE=.807019                     SLOPE=.961286
          INTERCEPT=.084548                 INTERCEPT=-.597987

SET*2     CC=.999985
          SLOPE=.777859
          INTERCEPT=.177779


METHYLENE CHLORIDE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                  AREA
         RATIO                      RATIO
1     ?.1                            ?1.373

2     ?.5                            ?3.797

3     ?2.5                           ?24.564

4     ?5                             ?47.641

5     ?10                            ?89.032

SET*1     CC=.998142              SET*3     CC=.999621
          SLOPE=.100682                     SLOPE=.116865
          INTERCEPT=3.54362E-02             INTERCEPT=-.447666

SET*2     CC=.999434
          SLOPE=.102742
          INTERCEPT=6.38037E-02
```

```
TRICHLOROFLUOROMETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
          CONCENTRATION                      AREA
              RATIO                          RATIO
1       ?.1                                   ?.781

2       ?.5                                   ?3.346

3       ?2.5                                  ?20.287

4       ?5                                    ?37.851

5       ?10                                   ?71.16

SET#1       CC=.999391           SET#3       CC=.999912
            SLOPE=.121239                    SLOPE=.147777
            INTERCEPT=4.66908E-02            INTERCEPT=-.535768

SET#2       CC=.998562
            SLOPE=.130489
            INTERCEPT=-7.66122E-03


1,1-DICHLOROETHENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
          CONCENTRATION                      AREA
              RATIO                          RATIO
1       ?.1                                   ?.373

2       ?.5                                   ?1.251

3       ?2.5                                  ?7.521

4       ?5                                    ?13.80

5       ?10                                   ?25.59

SET#1       CC=.999061           SET#3       CC=.999876
            SLOPE=.329537                    SLOPE=.416236
            INTERCEPT=.028795                INTERCEPT=-.675341

SET#2       CC=.997976
            SLOPE=.358604
            INTERCEPT=-3.14695E-02


1,1-DICHLOROETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
          CONCENTRATION                      AREA
              RATIO                          RATIO
1       ?.1                                   ?.457
```

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```
2      ?.5                                  ?1.425

3      ?2.5                                 ?9.641

4      ?5                                   ?18.114

5      ?10                                  ?33.80

SET#1      CC=.998193          SET#3      CC=.999811
           SLOPE=.254349                  SLOPE=.311486
           INTERCEPT=5.63798E-02          INTERCEPT=-.557855

SET#2      CC=.998478
           SLOPE=.269771
           INTERCEPT=4.26931E-02


TRANS-1,2-DICHLOROETHENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                         AREA
         RATIO                             RATIO
1      ?.1                                  ?.881

2      ?.5                                  ?3.851

3      ?2.5                                 ?22.079

4      ?5                                   ?41.692

5      ?10                                  ?78.04

SET#1      CC=.99965           SET#3      CC=.99914
           SLOPE=.111988                  SLOPE=.1425
           INTERCEPT=3.24982E-02          INTERCEPT=-.760179

SET#2      CC=.999079
           SLOPE=.119027
           INTERCEPT=-1.62767E-02


1,2-DICHLOROPROPANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                         AREA
         RATIO                             RATIO
1      ?.1                                  ?.088

2      ?.5                                  ?.269

3      ?2.5                                 ?1.437

4      ?5                                   ?2.641

5      ?10                                  ?5.185

SET#1      CC=.99948           SET#3      CC=.99991
           SLOPE=1.75517                  SLOPE=1.99553
           INTERCEPT=-1.62577E-02         INTERCEPT=-.328209
```

```
SET*2      CC=.998471
           SLOPE=1.89805
           INTERCEPT=-8.36138E-02


TRANS-1,3-DICHLOROPROPENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                     AREA
          RATIO                         RATIO
1       ?.1                              ?.123

2       ?.5                              ?.42

3       ?2.5                             ?2.152

4       ?5                               ?4.111

5       ?10                              ?7.897

SET*1      CC=.999795              SET*3     CC=.999964
           SLOPE=1.17315                     SLOPE=1.30753
           INTERCEPT=-2.05468E-02            INTERCEPT=-.338228

SET*2      CC=.999592
           SLOPE=1.22042
           INTERCEPT=-5.20236E-02


TRICHLOROETHENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                     AREA
          RATIO                         RATIO
1       ?.1                              ?.170

2       ?.5                              ?.586

3       ?2.5                             ?3.099

4       ?5                               ?5.461
-       ---                              -- ---


1,1,2-TRICHLOROETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                     AREA
          RATIO                         RATIO
1       ?.1                              ?.045

2       ?.5                              ?.166
-       -- -                             - ---
```

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```
3      ?2.5                             ?.931

4      ?5                               ?1.656

5      ?10                              ?2.901

SET#1      CC=.999552          SET#3      CC=.999244
           SLOPE=2.67521                  SLOPE=3.82981
           INTERCEPT=.014969              INTERCEPT=-1.17268

SET#2      CC=.996836
           SLOPE=3.0164
           INTERCEPT=-.101389


CIS-1,3-DICHLOROPROPENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                     AREA
         RATIO                         RATIO
1      ?.1                              ?.05

2      ?.5                              ?.264

3      ?2.5                             ?1.403

4      ?5                               ?2.623

5      ?10                              ?4.973

SET#1      CC=.999964          SET#3      CC=.999956
           SLOPE=1.76789                  SLOPE=2.10445
           INTERCEPT=2.15103E-02          INTERCEPT=-.479302

SET#2      CC=.999022
           SLOPE=1.90926
           INTERCEPT=-6.35816E-02


1,1,2,2-TETRACHLOROETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                     AREA
         RATIO                         RATIO
1      ?.1                              ?.336

2      ?.5                              ?1.068

3      ?2.5                             ?5.336

4      ?5                               ?8.219

5      ?10                              ?14.379

SET#1      CC=.999868          SET#3      CC=.999871
           SLOPE=.47687                   SLOPE=.826583
           INTERCEPT=-4.12149E-02         INTERCEPT=-1.86326

SET#2      CC=.984878
           SLOPE=.619814
```

```
CHLOROBENZENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                  AREA
          RATIO                      RATIO
1      ?.1                            ?2.094

2      ?.5                            ?8.073

3      ?2.5                           ?44.064

4      ?5                             ?67.357

5      ?10                            ?134.149

SET*1      CC=.999709            SET*3      CC=.99666
           SLOPE=5.66199E-02                SLOPE=8.13955E-02
           INTERCEPT=9.81589E-03            INTERCEPT=-.829434

SET*2      CC=.982548
           SLOPE=7.41694E-02
           INTERCEPT=-.287602
```

```
CHLOROFORM

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                        AREA
          RATIO                           RATIO
1      ?.1                                 ?.71

2      ?.5                                 ?2.138

3      ?2.5                                ?13.553

4      ?5                                  ?25.108

5      ?10                                 ?45.859

SET*1      CC=.998511           SET*3      CC=.999629
           SLOPE=.182399                   SLOPE=.233199
           INTERCEPT=3.61562E-02           INTERCEPT=-.736662

SET*2      CC=.998168
           SLOPE=.195949
           INTERCEPT=1.81877E-03


1,2-DICHLOROETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                        AREA
          RATIO                           RATIO
1      ?.1                                 ?.123

2      ?.5                                 ?.474

3      ?2.5                                ?2.896

4      ?5                                  ?5.195

5      ?10                                 ?9.9

SET*1      CC=.999212           SET*3      CC=.999985
           SLOPE=.850922                   SLOPE=1.06962
           INTERCEPT=4.25766E-02           INTERCEPT=-.581155

SET*2      CC=.996873
           SLOPE=.952052
           INTERCEPT=-5.14429E-02


1,1,1-TRICHLOROETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
     CONCENTRATION                        AREA
          RATIO                           RATIO
```

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
DROPPED HEAD BEGIN SECTIONS HERE
BEGIN LAST LINE OF TEXT

```
1       ?.1                             ?.728

2       ?.5                             ?2.257

3       ?2.5                            ?13.898

4       ?5                              ?26.455

5       ?10                             ?45.616

SET*1     CC=.998758             SET*3      CC=.997515
          SLOPE=.17829                      SLOPE=.238483
          INTERCEPT=2.99765E-02             INTERCEPT=-1.00071

SET*2     CC=.999109
          SLOPE=.186138
          INTERCEPT=2.28922E-02


CARBON TETRACHLORIDE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                     AREA
          RATIO                         RATIO
1       ?.1                              ?.648

2       ?.5                              ?1.898

3       ?2.5                             ?13.959

4       ?5                               ?25.417

5       ?10                              ?43.288

SET*1     CC=.997477             SET*3      CC=.997918
          SLOPE=.174479                     SLOPE=.257823
          INTERCEPT=7.34068E-02             INTERCEPT=-1.27091

SET*2     CC=.996892
          SLOPE=.191111
          INTERCEPT=3.73588E-02


BROMODICHLOROMETHANE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                     AREA
          RATIO                         RATIO
1       ?.1                              ?.137

2       ?.5                              ?.574

3       ?2.5                             ?2.515

4       ?5                               ?4.077

5       ?10                              ?8.181

SET*1     CC=.99985              SET*3      CC=.997995
```

```
                SLOPE=1.01567                           SLOPE=1.30229
                INTERCEPT=-5.88538E-02                  INTERCEPT=-.5796

      SET*2     CC=.992016
                SLOPE=1.27449
                INTERCEPT=-.377671


      TRICHLOROETHENE

      HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

      WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

      REMEMBER, WHEN INPUTTING CALIBRATION CURVES
      INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
      TO THE HIGHEST.
           CONCENTRATION                    AREA
               RATIO                        RATIO
      1     ?.1                              ?.170

      2     ?.5                              ?.586

      3     ?2.5                             ?3.099

      4     ?5                               ?5.161

      5     ?10                              ?8.848

      SET*1     CC=.999699           SET*3      CC=.999598
                SLOPE=.811163                   SLOPE=1.31064
                INTERCEPT=-9.01060E-03          INTERCEPT=-1.64083

      SET*2     CC=.992699
                SLOPE=.976851
                INTERCEPT=-.213742

      DO YOU WANT A PLOT OF  THESE POINTS?


      DIBROMOCHLOROMETHANE

      HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

      WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

      REMEMBER, WHEN INPUTTING CALIBRATION CURVES
      INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
      TO THE HIGHEST.
           CONCENTRATION                    AREA
               RATIO                        RATIO
      1     ?.1                              ?.08

      2     ?.5                              ?.328

      3     ?2.5                             ?1.948

      4     ?5                               ?3.378

      5     ?10                              ?5.663

      SET*1     CC=.999434           SET*3      CC=.998317
                SLOPE=1.26672                   SLOPE=2.03455
                INTERCEPT=3.85372E-02           INTERCEPT=-1.61921

      SET*2     CC=.995003
                SLOPE=1.4701
                INTERCEPT=-.10399


      BENZENE
```

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```
HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
         CONCENTRATION                          AREA
                RATIO                           RATIO
1          ?.1                                    ?.331

2          ?.5                                    ?1.325

3          ?2.5                                   ?6.598

4          ?5                                     ?11.669

5          ?10                                    ?21.629


SET*1       CC=.999967             SET*3        CC=.999989
            SLOPE=.381742                       SLOPE=.49939
            INTERCEPT=-1.69674E-02              INTERCEPT=-.807893

SET*2       CC=.997164
            SLOPE=.434665
            INTERCEPT=-.171984



BROMOFORM

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
         CONCENTRATION                          AREA
                RATIO                           RATIO
1          ?.1                                    ?.038

2          ?.5                                    ?.164

3          ?2.5                                   ?.754

4          ?5                                     ?1.225

5          ?20                                    ?2.142


SET*1       CC=.999956             SET*3        CC=.999978
            SLOPE=3.36378                       SLOPE=5.41018
            INTERCEPT=-3.85927E-02              INTERCEPT=-1.59845

SET*2       CC=.991727
            SLOPE=4.20603
            INTERCEPT=-.337844



TETRACHLOROETHENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
         CONCENTRATION                          AREA
                RATIO                           RATIO
1          ?.1                                    ?.955

2          ?.5                                    ?2.939
```

```
3      ?2.5                                      ?14.649

4      ?5                                        ?21.906

5      ?10                                       ?37.523

SET*1       CC=.999764              SET*3       CC=.999841
            SLOPE=.173712                       SLOPE=.326654
            INTERCEPT=-4.03782E-02              INTERCEPT=-2.23261

SET*2       CC=.980307
            SLOPE=.230948
            INTERCEPT=-.37369


TOLUENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                           AREA
          RATIO                               RATIO
1      ?.1                                     ?3.254

2      ?.5                                     ?10.194

3      ?2.5                                    ?49.729

4      ?5                                      ?81.43

5      ?10                                     ?151.546

SET*1       CC=.99985               SET*3       CC=.999703
            SLOPE=.051281                       SLOPE=7.32728E-02
            INTERCEPT=-4.65927E-02              INTERCEPT=-1.07152

SET*2       CC=.991887
            SLOPE=6.26604E-02
            INTERCEPT=-.285747


ETHYLBENZENE

HOW MANY POINTS DO YOU HAVE (MIN-3,MAX-6)?5

WHAT IS TODAY'S DATE(MAX.9 CHARACTERS).........?031583

REMEMBER, WHEN INPUTTING CALIBRATION CURVES
INPUT THE LOWEST FIRST AND GO SEQUENTIALLY
TO THE HIGHEST.
      CONCENTRATION                           AREA
          RATIO                               RATIO
1      ?.1                                     ?3.165

2      ?.5                                     ?10.443

3      ?2.5                                    ?46.251

4      ?5                                      ?83.791

5      ?10                                     ?163.741

SET*1       CC=.999997              SET*3       CC=.999883
            SLOPE=5.57509E-02                   SLOPE=6.36319E-02
            INTERCEPT=-7.90635E-02              INTERCEPT=-.39799

SET*2       CC=.998729
```

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REPRESENTATIVE OIL SAMPLE: RAW DATA AND CALCULATIONS FOR GC/MS ANALYSIS FOR VOLATILE ORGANICS

- Tetraglyme extract is spiked into organic-free laboratory water for analysis by GC/MS.
- Extracted ion areas for all detected analytes are measured. Area ratios are computed for the extracted ion of the analyte versus that for the closest eluting standard.
- Area ratios are entered into a computer program which provides the concentration of the analytes in the water purged, based upon the established calibration curves.
- Oil sample concentrations are calculated using equation provided in the example below.

For GCA 29661:

1. 0.9765g oil sample was extracted with 20 ml tetraglyme.
2. 20 µl of extract was spiked into 25 ml organic-free water. Internal standards were added at a concentration of 20 µg/l.
3. Extracted ion areas were measured and area ratios computed. Concentrations of analytes in the purged water sample was provided by the computer program.
4. The concentrations of analytes in the original oil sample were calculated. As an example, benzene was found to be in the water purged at a level of 23 µg/l. Calculation of the original sample concentration was done as shown:

$$\begin{array}{c}\text{Oil sample benzene}\\ \text{concentration } (\mu g/g)\end{array} = \frac{23\ \mu g/l \text{ water} \times 0.025 \text{ l water} \times 20 \text{ ml tetraglyme extract}}{\begin{array}{c}.020 \text{ ml tetraglyme}\\ \text{extract purged}\end{array} \times \begin{array}{c}0.9765g \text{ oil sample}\\ \text{extracted}\end{array}}$$

$$= 590\ \mu g/g = 590 \text{ mg/kg}$$

5. Detection limits for the sample were calculated as shown:

$$\begin{array}{c}\text{Detection limit}\\ \text{(priority pollutants)}\end{array} = \frac{.010\ \mu g \text{ (method limit)} \times 20 \text{ ml tetraglyme extract}}{.020 \text{ ml tetraglyme purged} \times 0.9765g \text{ oil}}$$

$$= 10\ \mu g/g = 10 \text{ mg/kg}$$

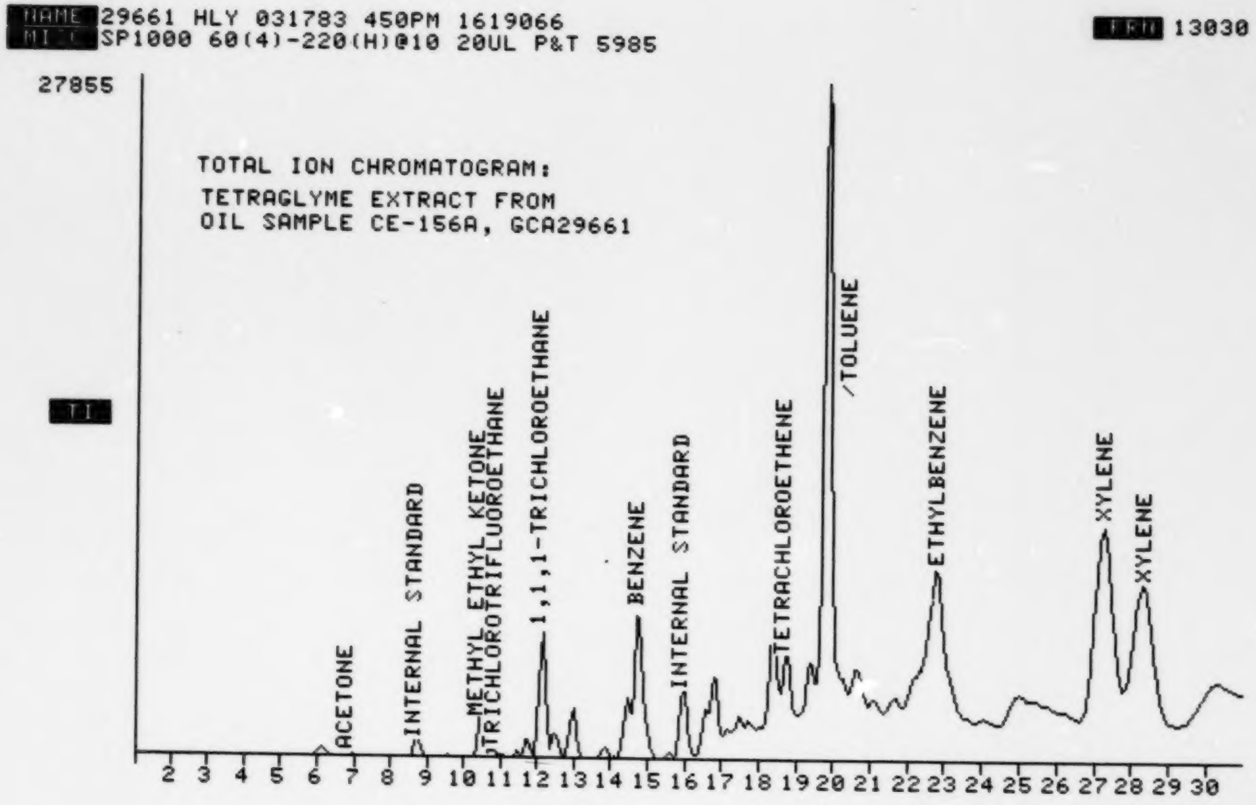

Figure C-12. Oil sample.

PRIORITY POLLUTANT REPORT SHEET
VOLATILE ORGANIC COMPOUNDS

SAMPLE NUMBER 29661
DESCRIPTION TETRAGLYME:20UL
DATE 031783
PROJECT* 1619066

COMPOUND	CONCENTRATION
METHYLENE CHLORIDE	TRACE
1,1,1-TRICHLOROETHANE	37
BENZENE	23
TETRACHLOROETHENE	5.3
TOLUENE	310
ETHYLBENZENE	97
ACETONE	100
TRICHLOROTRIFLUOROETHANE	TRACE
METHYL ETHYL KETONE	390

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```
NAME 29661 HLY 031783 450PM 1619066                    FRN 13030

AREA TABLE ENTRIES: FRN 13030

Entry  Time    Mass          Area        %

  1     8.7   127.7          747.     100.0
  2     6.1    83.7          804.     ~~107.5~~
  3    10.8   100.7          191.      25.6
  4    10.5    71.7          590.      78.9
  5     7.0    42.7          312.      41.8
  6    12.1    96.7         7582.    1014.6
CALCULATE % ON ENTRY #:
AREA TABLE ENTRIES: FRN 13030

Entry  Time    Mass          Area        %

  1    16.0    76.7         2205.     100.0
  2    14.8    77.7         6829.     309.7
CALCULATE % ON ENTRY #:
AREA TABLE ENTRIES: FRN 13030

Entry  Time    Mass          Area        %

  1    19.0    54.7          217.     100.0
  2    18.8   165.7          383.     176.4
  3    19.8    90.7        49069.   22571.8
  4    22.8    90.7        17817.    8195.7
  5    27.8    90.7        64448.   29646.2
CALCULATE % ON ENTRY #:
```

Bl. correction

82.7

29661

20ul tetraglyme

APPENDIX D

GC/MS DATA

Project 1-619-066 GCA Control No. 29639

DATA REPORT SHEET

Purgeables

Sample I.D. 10683 Analysis Date 3/16/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene		ND	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	440	
chlorobenzene		ND	
ethylbenzene	91	240	

ND = < 20 mg/kg
ND* = < 900 mg/kg

Project 1-619-066 GCA Control No. 29639

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 10683 Analysis Date 3/16/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	590	

ND = < 2000 mg/kg
ND* = < 20 mg/kg

Project 1-619-066

GCA Control No. 29641

DATA REPORT SHEET

Purgeables

Sample I.D. 10692

Analysis Date 4/13/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	Trace	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	23	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	87	
chlorobenzene		ND	
ethylbenzene	91	94	

ND = < 1 mg/kg
Trace = < 5 mg/kg
ND* = < 50 mg/kg

Project 1-619-066 GCA Control No. 29641

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 10692 Analysis Date 4/13/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	67	

ND = < 100 mg/kg
ND* = < 1 mg/kg

Project 1-619-066

GCA Control No. 29642

DATA REPORT SHEET

Purgeables

Sample I.D. 12010

Analysis Date 3/21/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene		ND	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene		ND	
chlorobenzene		ND	
ethylbenzene		ND	

ND = < 2 mg/kg
ND* = < 80 mg/kg

Project 1-619-066

GCA Control No. 29642

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 12010

Analysis Date 3/21/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	22	

ND = < 200 mg/kg
ND* = < 2 mg/kg

Project 1-619-066 GCA Control No. 29643

DATA REPORT SHEET

Purgeables

Sample I.D. 16375 Analysis Date 4/13/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	Trace	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	15	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	49	
chlorobenzene		ND	
ethylbenzene	91	47	

ND = < 0.9 mg/kg
Trace = < 4 mg/kg
ND* = < 40 mg/kg

Project 1-619-066 GCA Control No. 29643

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 16375 Analysis Date 4/13/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	47	

ND = < 90 mg/kg
ND* = < 0.9 mg/kg

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Project 1-619-066 GCA Control No. 29646

DATA REPORT SHEET

Purgeables

Sample I.D. 16379 Analysis Date 4/13/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane	63	Trace	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	Trace	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	46	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	230	
chlorobenzene		ND	
ethylbenzene	91	160	

ND = < 1 mg/kg
Trace = < 5 mg/kg
ND* = < 50 mg/kg

Project 1-619-066

GCA Control No. 29646

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 16379

Analysis Date 4/13/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	**Remarks**
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	110	

ND = < 100 mg/kg
ND* = < 1 mg/kg

Project 1-619-066 GCA Control No. 29649

DATA REPORT SHEET

Purgeables

Sample I.D. 19028 Analysis Date 4/13/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	30	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	Trace	
1,1,2,2-tetrachloroethane		ND	
toluene	91	40	
chlorobenzene		ND	
ethylbenzene	91	30	

ND = < 1 mg/kg
Trace = < 5 mg/kg
ND* = < 50 mg/kg

Project 1-619-066 GCA Control No. 29649

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 19028 Analysis Date 4/13/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	**Remarks**
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	36	

ND = < 100 mg/kg
ND* = < 1 mg/kg

Project 1-619-066 GCA Control No. 29652

DATA REPORT SHEET

Purgeables

1

Sample I.D. 19190 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	28	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	110	
chlorobenzene		ND	
ethylbenzene	91	110	

ND = < 1 mg/kg
ND* = < 40 mg/kg

Project 1-619-066

GCA Control No. 29652

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 19190

Analysis Date 4/11/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	50	

ND = < 100 mg/kg
ND* = < 1 mg/kg

Project 1-619-066 GCA Control No. 29656

DATA REPORT SHEET

Purgeables

Sample I.D. 20327 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	15	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	100	
chlorobenzene		ND	
ethylbenzene	91	21	

ND = < 0.9 mg/kg
ND* = < 40 mg/kg

Project 1-619-066 GCA Control No. 29656

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 20327 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	20	

ND = < 90 mg/kg
ND* = < 0.9 mg/kg

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Project 1-619-066 GCA Control No. 29657

DATA REPORT SHEET

Purgeables

Sample I.D. 20328 Analysis Date 9/8/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	110	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	910	
chlorobenzene		ND	
ethylbenzene	91	970	

ND = < 2 mg/kg
ND* = < 90 mg/kg

Project 1-619-066 GCA Control No. 29657

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 20328 Analysis Date 9/8/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	4100	

ND = < 200 mg/kg
ND* = < 2 mg/kg

Project 1-619-066 GCA Control No. 29659

DATA REPORT SHEET

Purgeables

Sample I.D. 22621 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane		ND	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	45	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	110	
chlorobenzene		ND	
ethylbenzene	91	120	

ND = <1 mg/kg
ND* = < 40 mg/kg

Project 1-619-066 GCA Control No. 29659

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 22621 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	79	

ND = < 100 mg/kg
ND* = < 1 mg/kg

Project 1-619-066 GCA Control No. 29660

DATA REPORT SHEET

Purgeables

Sample I.D. 22623 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride	84	11	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	8.0	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	37	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	330	
chlorobenzene		ND	
ethylbenzene	91	230	

ND = < 1 mg/kg
ND* = < 40 mg/kg

Project 1-619-066 GCA Control No. 29660

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 22623 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	180	

ND = < 100 mg/kg
ND* = < 1 mg/kg

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Project 1-619-066 GCA Control No. 29661

DATA REPORT SHEET

Purgeables

Sample I.D. CE 156A Analysis Date 3/17/83, 4/7/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	950	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	590	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	140	
1,1,2,2-tetrachloroethane		ND	
toluene	91	7900	
chlorobenzene		ND	
ethylbenzene	91	2500	

ND = < 10 mg/kg

ND* = < 500 mg/kg

Project 1-619-066 GCA Control No. 29661

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. CE 156A Analysis Date 3/17/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone	43	2600	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone	72	9900	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane	101	Trace	
xylene (isomers)	91	7000	

ND = < 1000 mg/kg
Trace = < 40 mg/kg

Project 1-619-066 GCA Control No. 29663

DATA REPORT SHEET

Purgeables

Sample I.D. CE 158A Analysis Date 4/13/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride	84	180	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane	101	14	
1,1-dichloroethylene	96	49	
1,1-dichloroethane	63	Trace	
trans-1,2-dichloroethylene	96	Trace	
chloroform	83	10	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	1900	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	170	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	140	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	140	
1,1,2,2-tetrachloroethane		ND	
toluene	91	490	
chlorobenzene		ND	
ethylbenzene	91	240	

ND = < 2 mg/kg
Trace = < 9 mg/kg
ND* = < 90 mg/kg

Project 1-619-066

GCA Control No. 29663

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. CE 158A

Analysis Date 4/13/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane	101	26	
xylene (isomers)	91	160	

ND = < 200 mg/kg
ND* = < 2 mg/kg

Project 1-619-066 GCA Control No. 29665

DATA REPORT SHEET

Purgeables

Sample I.D. ES - 821203 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride	84	15	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane	101	510	
1,1-dichloroethylene	96	15	
1,1-dichloroethane	63	Trace	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane	62	8.4	
1,1,1-trichloroethane	97	970	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	5.6	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	55	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	39	
1,1,2,2-tetrachloroethane		ND	
toluene	91	480	
chlorobenzene		ND	
ethylbenzene	91	190	

ND = < 0.7 mg/kg
Trace = < 3 mg/kg
ND* = < 30 mg/kg

Project 1-619-066 GCA Control No. 29665

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. ES - 821203 Analysis Date 4/11/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	110	

ND = < 70 mg/kg
ND* = < 0.7 mg/kg

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Project 1-619-066

GCA Control No. 29666

DATA REPORT SHEET

Purgeables

Sample I.D. ES - 821204

Analysis Date 4/13/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene	96	42	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	17	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	440	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene		ND	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	3500	
1,1,2,2-tetrachloroethane		ND	
toluene		ND	
chlorobenzene		ND	
ethylbenzene	91	50	

ND = < 3 mg/kg
ND* = < 100 mg/kg

Project 1-619-066

GCA Control No. 29666

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. ES - 821204

Analysis Date 4/13/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	93	

ND = < 300 mg/kg
ND* = < 3 mg/kg

Project 1-619-066 GCA Control No. 29669

DATA REPORT SHEET

Purgeables

Sample I.D. ES - 821208 Analysis Date 3/21/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride	84	730	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane	101	Trace	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform	83	130	
1,2-dichloroethane	62	76	
1,1,1-trichloroethane	97	1400	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	450	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	520	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	940	
1,1,2,2-tetrachloroethane		ND	
toluene	91	60000	
chlorobenzene		ND	
ethylbenzene	91	7000	

ND = < 10 mg/kg
Trace = < 40 mg/kg
ND* = < 400 mg/kg

Project 1-619-066 GCA Control No. 29669

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. ES - 821208 Analysis Date 3/17/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone	43	11000	
butyl acetate	73	9100	
ethyl acetate		ND	
methyl ethyl ketone	72	34000	
methyl isobutyl ketone	85	17000	
1,1,2-trichloro-1,2,2-trifluoroethane	101	370	
xylene (isomers)	91	35000	

ND = < 1000 mg/kg

Project 1-619-066 GCA Control No. 29670

DATA REPORT SHEET

Purgeables

Sample I.D. ES - 821219 Analysis Date 3/17/83, 3/21/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride	84	3000	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane	63	210	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	28000	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene	130	14000	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	Trace	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	21000	
1,1,2,2-tetrachloroethane		ND	
toluene	91	81000	
chlorobenzene		ND	
ethylbenzene	91	3900	

ND = < 20 mg/kg
Trace = < 100 mg/kg
ND* = < 1000 mg/kg

Project 1-619-066 GCA Control No. 29670

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. ES - 821219 Analysis Date 3/17/83, 3/21/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone	72	95000	
methyl isobutyl ketone	85	18000	
1,1,2-trichloro-1,2,2-trifluoroethane	101	320	
xylene (isomers)	91	19000	

ND = < 2000 μg/kg

Project 1-619-066 GCA Control No. 29675

DATA REPORT SHEET

Purgeables

Sample I.D. WH 187A Analysis Date 3/17/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	270	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	Trace	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	490	
1,1,2,2-tetrachloroethane		ND	
toluene	91	1300	
chlorobenzene		ND	
ethylbenzene	91	630	

ND = < 20 mg/kg

Trace = < 90 mg/kg

ND* = < 900 mg/kg

Project 1-619-066 GCA Control No. 29675

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. WH 187A Analysis Date 3/17/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	2700	

ND = < 2000 mg/kg
ND* = < 20 mg/kg

Project 1-619-066

GCA Control No. 29676

DATA REPORT SHEET

Purgeables

Sample I.D. WH 188A

Analysis Date 3/17/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	420	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	Trace	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene	166	310	
1,1,2,2-tetrachloroethane		ND	
toluene	91	1800	
chlorobenzene		ND	
ethylbenzene	91	800	

ND = < 20 mg/kg
Trace = < 80 mg/kg
ND* = < 800 mg/kg

Project 1-619-066　　GCA Control No. 29676

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. WH 188A　　Analysis Date 3/17/83

Sample Matrix Oil　　Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	3300	

ND = < 2000 mg/kg
ND* = < 20 mg/kg

Project 1-619-066

GCA Control No. 29679

DATA REPORT SHEET

Purgeables

Sample I.D. 9 - 121 - 12 - 10 - 82 - 4

Analysis Date 3/17/83

Sample Matrix Oil

Instrument HP 5985 GC/MS

Parameter	Ion Used To Quantitate	Concentration (mg/kg)	Remarks
chloromethane		ND	
dichlorodifluoromethane		ND	
bromomethane		ND	
vinyl chloride		ND	
chloroethane		ND	
methylene chloride		ND	
acrolein		ND*	
acrylonitrile		ND*	
trichlorofluoromethane		ND	
1,1-dichloroethylene		ND	
1,1-dichloroethane		ND	
trans-1,2-dichloroethylene		ND	
chloroform		ND	
1,2-dichloroethane		ND	
1,1,1-trichloroethane	97	3900	
carbon tetrachloride		ND	
bromodichloromethane		ND	
bis-chloromethyl ether		ND	
1,2-dichloropropane		ND	
trans-1,3-dichloropropene		ND	
trichloroethylene		ND	
dibromochloromethane		ND	
cis-1,3-dichloropropene		ND	
1,1,2-trichloroethane		ND	
benzene	78	Trace	
2-chloroethylvinyl ether		ND	
bromoform		ND	
tetrachloroethene		ND	
1,1,2,2-tetrachloroethane		ND	
toluene	91	730	
chlorobenzene		ND	
ethylbenzene	91	580	

ND = < 20 mg/kg
Trace = < 100 mg/kg
ND* = < 1000 mg/kg

Project 1-619-066 GCA Control No. 29679

Data Report Sheet
Nonpriority Pollutant Purgeables

Sample I.D. 9 - 121 - 12 - 10 - 82 - 4 Analysis Date 3/17/83

Sample Matrix Oil Instrument HP 5985 GC/MS

Parameter	Ion Used to Quantitate	Concentration (mg/kg)	Remarks
acetone		ND	
butyl acetate		ND	
ethyl acetate		ND	
methyl ethyl ketone		ND	
methyl isobutyl ketone		ND	
1,1,2-trichloro-1,2,2-trifluoroethane		ND*	
xylene (isomers)	91	1900	

ND = < 2000 mg/kg
ND* = < 20 mg/kg

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APPENDIX E

GCA QUALITY ASSURANCE PROJECT PLAN CONTAMINATED HEATING OILS

QA 010

EPA CONTRACT NO. 68-02-3168
TECHNICAL SERVICE AREA 2
WORK ASSIGNMENT NO. 66
(GCA 1-619-066/566)

REVISED
QUALITY ASSURANCE PROJECT PLAN FOR COMPARATIVE ANALYSIS OF CONTAMINATED HEATING OILS

APPROVAL:

GCA Program Manager Thomas G. Hepper Date 2/17/83

GCA Assignment Manager Robert R. Hall Date 2/18/83

GCA QA Manager Rose Mary Ellersick Date 2/17/83

EPA Project Officer ______________________ Date __________

EPA QA Officer ______________________ Date __________

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1.0 PROJECT DESCRIPTION

1.1 OVERVIEW

Investigations by the news media have indicated that some heating oils may be contaminated with potentially hazardous wastes. Disposal of hazardous wastes in high temperature incinerators is expensive. Mixing the wastes with heating oil offers a double payoff; the disposal fee is eliminated and the wastes are sold at a profit. It is suspected that this practice will be most likely to occur with oil sold to large apartment complexes and office buildings in metropolitan areas. EPA is concerned about the potential for emissions of unburned toxic chemicals in densely populated areas.

The potential problem of heating oil contamination has been investigated by using the available technical literature and by conducting discussions with many industry and government representatives. One conclusion of this phase of the program was that New York City would be a good study area. Work was started to develop a statistically valid sampling strategy. The number of oil storage tanks and the locations of some tanks were determined from information provided by the New York City Department of Environmental Protection and the New York State Department of Environmental Conservation. The size distribution of the tanks was determined from data provided by the New York City Fire Department. Dr. James Dunn of the University of Arkansas, used the above data and some necessary assumptions to develop a statistically valid sampling strategy.[7]

The statistical analyses showed that a very large number of samples (see Table 1 as an example) would be needed to define the extent of heating oil contamination. It has, therefore, been necessary to redefine the program objectives. A meeting was held with EPA Region II, IERL/RTP, New York City, New York State and New Jersey representatives on December 3, 1982 to discuss their current regulatory development efforts and sampling programs. As a result of this meeting, additional data requirements of mutual interest were identified.

One concern is that some samples of virgin oil contain higher than expected levels of chlorine. The chlorine may result from contamination by salt water or may consist of organic chlorine compounds. However, no data

TABLE 1-1. MINIMUM SAMPLE SIZES (n) FOR ESTIMATION OF THE FRACTION OF CONTAMINATED #6 FUEL OIL

$$n \geq n_0/(1 + n_0/N),$$

where $n_0 = z^2(1 - P)[1 + c^2(x)]/d^2PP_{\#6}$,

$z = 1.96$,

$c(x) = 0.81415$ = coefficient of variation

$P_{\#6} = 0.5879$ = fraction of tanks that contain #6 oil

$N = 32400$ = number of storage tanks

	Maximum Relative Error (d)			
P	0.1	0.2	0.3[a]	0.4
0.00333	29454	23141	17050	12459
0.01	24883	14671	8412	5554
0.03[a]	16831	6983	3474[a]	2051
0.06	11137	3752	1782	1027
0.09	8186	2525	1173	670
0.12	6380	3538	859	489

[a] Example: If we assume that 3 percent of the tanks contain contaminated oil and are willing to accept a relative error of ± 30 percent, then we would have to plan to collect 3474 samples.

are currently available. Therefore, the current objective of this study is to provide some indication of whether the chlorine in some example samples is present in inorganic or organic compounds. In addition, we plan to analyze for selected volatile organic compounds that could represent a source of organic chlorine contamination. (See Table 2)

Samples of heating oil and waste oil have been collected by the New York State Department of Environmental Conservation (NYSDEC), the New York City Department of Environmental Protection (NYCDEP), and the New Jersey Department of Environmental Protection (NJDEP). The NYCDEP and the NJDEP samples have been analyzed for chlorine and other elements and physical properties by Engineering Sciences under Contract No. 68-01-6312, Work Assignment No. 68 from the EPA Division of Stationary Source Compliance. Samples that contain levels of chlorine appropriate to the goals of this project will be selected for analysis.

Three types of analyses will be conducted:

1. Cl, Br, F by ion chromatography
2. Volatile organic compounds by purge and trap GC/MS procedures
3. Total organic halogens in water extracts with a Dohrmann DX-20 Total Organic Halide Analyzer

Oil samples will be prepared for the ion chromatography work by Parr Bomb Combustion (ASTM D808-63). Oil samples will also be mixed with water and separated into two phases. The separation procedure will be similar to ASTM D878-65 (Standard Test Method for Inorganic Chlorides and Sulfates in Insulating Oils). The water phase (which should contain inorganic halogens) will be analyzed for Cl, Br, and F by ion chromatography and total organic halides with the Dohrmann DX-20.[1] This latter analysis will determine whether or not the water phase contains only inorganic halogens. Samples for volatile analysis will be prepared by employing a Modified Method A101b (Sampling and Analysis Manual for Hazardous Waste Incineration)[2] with subsequent analysis by GC/MS procedures outlined in Method 624.[5]

TABLE 1-2. VOLATILE ORGANIC COMPOUNDS SELECTED FOR ANALYSIS

Chlorinated Compounds

- Carbon tetrachloride
- Chlorobenzene
- Chloroform
- Dibromochloromethane
- Dichlorodifluoromethane
- 1,1-dichloroethane
- 1,2-dichloroethane
- 1,2-dichloroethylene
- 1,2-dichloropropane
- Methyl chloride
- Methylene chloride
- 1,1,2,2-tetrachloroethane
- 1,1,1-trichloroethane
- 1,1,2-trichloroethane
- Trichloroethene
- Trichlorofluoromethane
- 1,1,2-trichloro-1,2,2-trifluoroethane
- Vinyl chloride

Other Volatile Compounds

- Acetone
- Benzene
- Butyl acetate
- Ethyl acetate
- Ethyl benzene
- Methyl ethyl ketone
- Methyl isobutyl ketone
- Toluene
- Xylene (isomers)

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

Figure 2-1 presents GCA's organization chart for this project showing the individuals responsible for each key element of the overall task. It should be noted that the QA Manager reports directly to the Division General Manager.

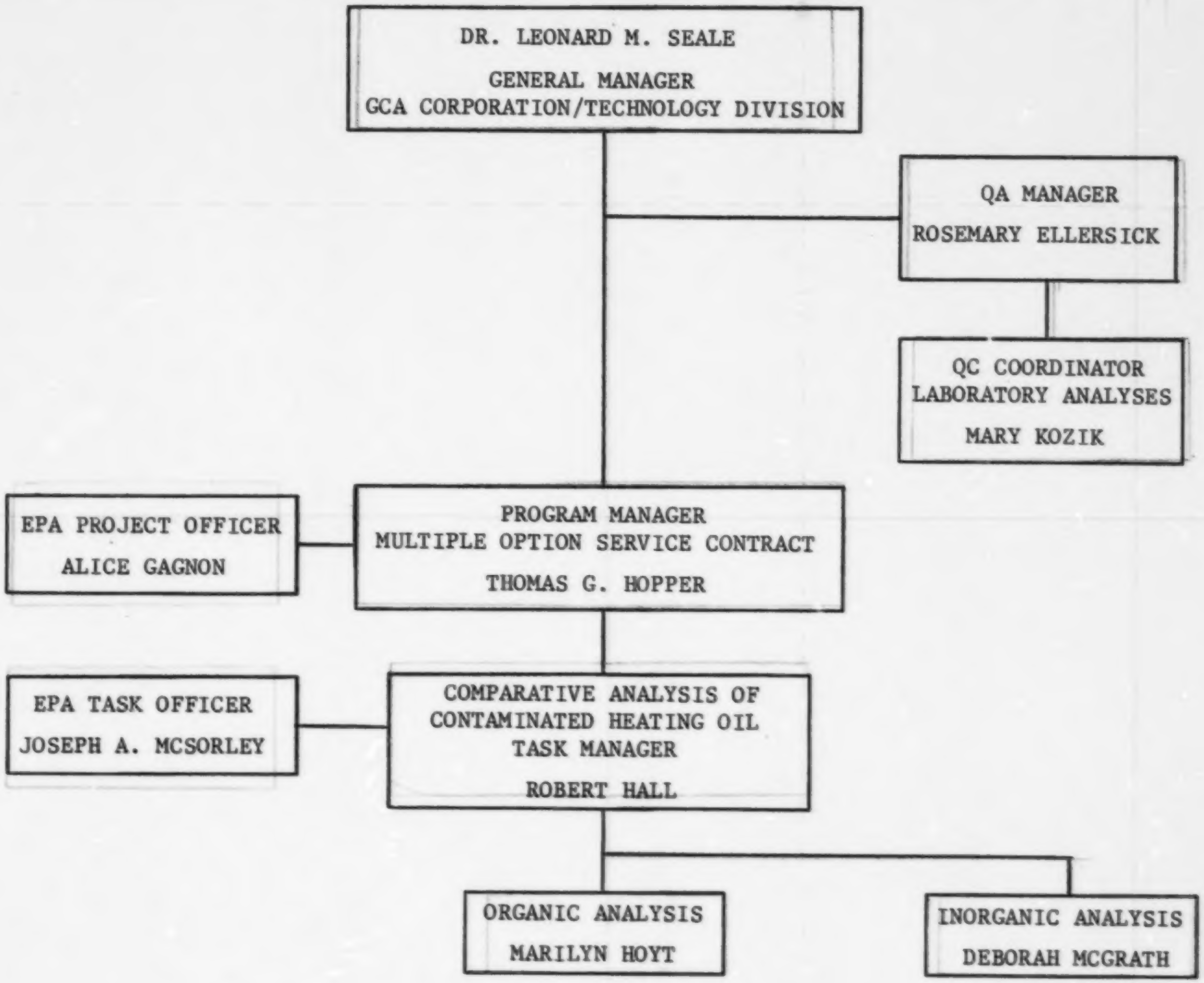
2.1 QA MANAGER'S RESPONSIBILITIES

The Division QA Manager is the responsible Quality Assurance Officer for this project. She will review and approve the QA Project Plan before it is submitted to EPA. She will ensure that any necessary revisions are made and she will check on implementation of the QA Plan during the life of the project, scheduling performance or system audits as necessary.

She will initiate or follow up on corrective actions and aid in preparation of a section of the Final Report summarizing QA/QC activities and including estimates of the precision, accuracy, and completeness of data achieved. Quality problems found and corrective actions taken will be described.

2.2 LABORATORY QC COORDINATOR'S RESPONSIBILITIES

The Laboratory Analysis Department QC Coordinator will oversee and implement the ongoing QC program within the department. She will ensure that the required QC procedures for this project are followed, initiate corrective actions as necessary, and maintain and report, on a monthly basis, the QC records and results for this project.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COMPARATIVE ANALYSIS OF
CONTAMINATED HEATING OIL
TASK MANAGER
ROBERT HALL
ORGANIC ANALYSIS
MARILYN HOYT
INORGANIC ANALYSIS
DEBORAH MCGRATH

Figure 2-1. Project organization and responsibility

3.0 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION ACCURACY, COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

The major measurement parameters are total halides, volatile organics, Cl, Br and F. Precision, accuracy and completeness goals for these measurements are presented in Table 3-1. These goals are based on previous experience in applying comparable procedures to a variety of complex sample matrices.

TABLE 3-1. PRECISION, ACCURACY AND COMPLETENESS GOALS

Measurement method	Precision (%)	Accuracy (%)	Completeness (%)
Volatile organics	25	±20	95
Cl, Br, F	10	±20	95
Total Halides	10	±20	95

Comparability of the measurement results on this program with other similar programs, as with measurements of the same heating oils made at another time, is ensured by the use of the written sampling and analytical methods presented or referenced in this QA Plan and by the use of standard reporting units. In general, all analytical results on the oil samples will be reported as mg/kg.

4.0 SAMPLING PROCEDURES

The samples have been collected by New York City, New York State and New Jersey. Sample collection and preservation procedures vary depending on which organization handled the samples. In addition, aliquots of some samples that were collected in 1-quart jars have been partially analyzed. The sample and preservation procedure will be defined by each organization and used in interpreting the analytical results.

5.0 SAMPLE CUSTODY

5.1 FIELD CUSTODY PROCEDURES

New York State, New York City and New Jersey have followed standard chain of custody procedures.

5.2 LABORATORY CUSTODY PROCEDURES

Upon delivery to GCA the samples and the SAMPLE PACKING SHEET will be turned over to the Sample Bank Manager (SBM) who:

- Logs the sample into a large bound Master Log
- Notes the condition and the container type
- Assigns and affixes GCA Control Number to the sample container
- Initiates a page for each sample in the Custody Book and makes sure that each handling of the sample is documented there.
- After necessary preservation and/or subdivision, stores the samples in the refrigerated or nonrefrigerated section of the Sample Bank as appropriate.

All withdrawals from and the returns to the Sample Bank are initiated by entry in the SAMPLE BANK TRANSACTIONS LOG BOOK (Figure 5-1). When sample preparation and analysis procedures necessitate the transfer of samples between two analysts within the Laboratory, a SAMPLE CUSTORY TRANSFER (Figure 5-2) form is required. When samples are transferred to an outside laboratory they must be accompanied by a RECEIPT OF SAMPLE FOR ANALYSIS form (Figure 5-3).

SAMPLE BANK TRANSACTIONS

REQUEST FOR SAMPLES			RETURN OF SAMPLES		
GCA Control Nos.	Date Needed	Signature	GCA Control Nos.	Date Returned	Signature

8/80

Figure 5-1. Sample bank transactions log book.

SAMPLE CUSTODY TRANSFER

PURPOSE

Procedure/Analysis required ______________________________

____

(General information only--analyst MUST refer to Project File for specific details.)

Instrumentation required ______________________________

BACKGROUND

Client ____

Contract (Charge) No. ______________ Work Order No. ____________

SAMPLES

General description of sample type(s) ______________________

____

List of samples (by GCA Control No.):

____

____

____

____

Additional samples (QC-blanks, QC-spikes, etc.):

____

____

Total number of samples ______________________________

Comments ______________________________________

____

TRANSFER

From ______________________________ Date ______________

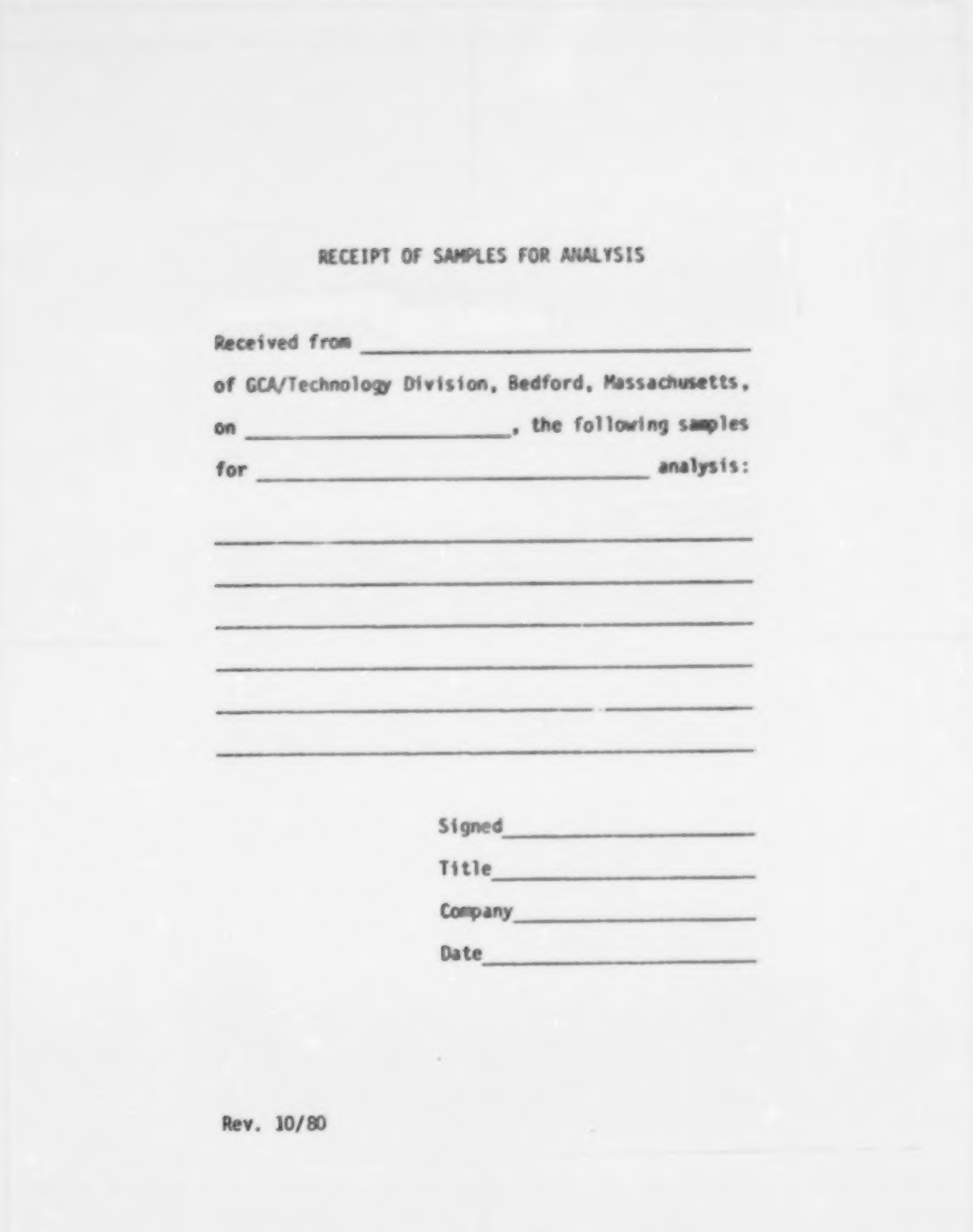
Received by __________________________ Date ______________

(Location of samples) ______________________________)

When completed, make 3 copies--one each for originator, receipient, and Task Manager.

RETURN ORIGINAL TO PROJECT FILE

Figure 5-2. Sample custody transfer.



RECEIPT OF SAMPLES FOR ANALYSIS

Received from ______________________________
of GCA/Technology Division, Bedford, Massachusetts,
on ____________________, the following samples
for ______________________________ analysis:

____
____
____
____
____
____

Signed____________________
Title____________________
Company____________________
Date____________________

Rev. 10/80

Figure 5-3. Receipt of samples for analysis.

6.0 CALIBRATION PROCEDURES AND FREQUENCY

6.1 DOHRMANN DX-20 TOTAL ORGANIC HALIDE ANALYZER SYSTEM

6.1.1 Calibration Standards

1. Prepare a stock solution of 2,4,6-trichlorophenol (Ultra Scientific, Reference Standard Grade) in methanol.

2. Prepare working standards daily by dilution of the stock solution with DI water to bracket expected sample concentrations.

6.1.2 Calibration Procedure

1. Follow appropriate startup procedures given in manufacturer's operating manual.[4]

2. Use three working standards at the start of each analysis day to check that the instrument is functioning properly.

3. Inject each standard into Dohrmann granular activated charcoal (GAC) in quartz boat. (Do not use adsorption columns.)

4. Follow routine operating procedures for the MC-1 Analyzer Module.[4]

5. Record the instrument readout in ug Cl and compare to known Cl content of each standard.

6. Verify the standards by injecting an EPA/EMSL QC Concentrate chloride sample.

7. If the instrument readouts are not within ±5 percent of the verified standard Cl content, clean and troubleshoot the instrument until this performance can be achieved.

6.2 HEWLETT PACKARD 5993 GC/MS

6.2.1 Calibration Standards

1. Purchase or prepare the stock solutions from the pure compound, store at 4°C, prepare fresh every 2 weeks or as needed.

2. Prepare the working standards by dilution of the stock standard using the appropriate solvent.

3. Verify the standards by analysis of an EPA QC sample or other appropriate Laboratory Control Sample.

6.2.2 Calibration Procedure

1. Tune the instrument daily to the criteria stated in EPA Method 624.[5]

2. Prepare a three- to five-point calibration curve every 2 weeks; the standard curve must be verified daily as described in Step 3.

3. Analyze an EPA QC sample or other appropriate Laboratory Control Sample. If the results are within the established control limits, analysis may proceed.

4. Document standard preparation in the Analyst's notebook. Enter all required information in instrument logbook; sign and date the entry.

6.3 DIONEX MODEL 14 ION CHROMATOGRAPH

6.3.1 Calibration Standards

1. Prepare the 1000 ppm stocks of chloride, bromide and flouride solution using sodium salts of all anions.

2. Prepare working standards in the range of 0.5-5.0 ppm by dilution of the stock solution.

3. Verify the working standards by analysis of a QC sample prepared from appropriate EPA concentrates where available.

6.3.2 Calibration Procedure

1. Set up the instrument according to the manufacturer's instructions.

2. Inject the blank and calibration standards and record the peak heights and retention times of each.

3. Analyze a QC sample prepared from an appropriate EPA concentrate; if the reported value is within 5 percent of the expected value, sample analysis may begin. Reanalyze the sample at the end of the analysis period or after every 10-15 samples if the instrument is running for an extended period.

4. Enter all information regarding instrument operating parameters and analysis of laboratory control samples in the instrument logbook; sign and date the entry. Standard preparation must be documented in the analyst's notebook.

7.0 ANALYTICAL PROCEDURES

The following sections present a summary of the analytical procedures to be used in this program. The QC data obtained from the use of surrogates, duplicates, and spiked samples will be used to monitor the performance of the sample preparation and analysis methods.

7.1 TOTAL ORGANIC HALIDES

Oil samples will be separated into water and oil fractions according to ASTM D878-65 described below:

> "3.1 In a 250-ml separatory funnel, shake thoroughly 100 ml of the oil with 75 ml of water at 203°F (95°C). Allow to separate, then draw off the water layer into a 250-ml beaker.
>
> "3.1.1 In case the separated water is not clear, filter it through a 10-cm diameter qualitative filter paper into a 250-ml beaker. The filtrate is then used for tests. As a check on the filter paper, 75 ml of hot water, passed through the paper prior to filtering the separated water, should give negative tests for chlorides and sulfates."

The water fraction is expected to contain inorganic halides (to be measured by ion chromatography), but it will be checked for organic halides with the Dohrmann DX-20 total organics halide analyzer.

The analytical procedure will follow the manufacturer's guidelines[4] and EPA Method 450.1 Interim.[1] Organic halides are defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the instrument operating conditions. Fluoride containing compounds are not determined. The halides are quantitated against chloride standards and reported as chloride. A summary of the procedure follows:

1. Pass the sample of water through a column containing 40 mg of activated carbon. Wash the column to remove any trapped inorganic halides.
2. Transfer the activated carbon column to the empty sample boat.

3. Pyrolyze the sample for 2 minutes at 200°C in a CO$_2$-rich atmosphere to ensure conversion of brominated trihalomethanes to a titratable species. Then pyrolyze the same sample at 800°C in an O$_2$-rich atmosphere to effect conversion of the less volatile sample components. High temperature pyrolysis may take from 6 to 10 minutes for completion.
4. Effluent gases from pyrolysis are directly analyzed in the microcoulometric-titration cell.
5. Record the instrument readout (total μg Cl in sample).
6. Calculate μg Cl in a gram of the oil sample and report as mg/kg.

7.2 VOLATILE ORGANICS

Analysis of the fuel feed for volatile organics will be accomplished using the purge and trap GC/MS procedure similar to Method A101b.[2] An aliquot of the fuel sample will be mixed with tetraglyme and a portion of this mixture transferred to the purging device. Method A101b specifies that the sample be mixed with polyethylene glycol but GCA has found that tetraglyme (tetraethylene glycol dimethyl ether) is easier to purify and therefore produces less interferences. The volatile components in the sample are transferred to the vapor phase by bubbling an inert gas through the solution at ambient temperature. The volatiles are trapped on a sorbent column and subsequently analyzed by GC/MS. Th GC/MS procedures are those outlined in Method 624[5] and cited in Method A101b.[2]

7.3 Cl, Br, F ANALYSIS

Oil samples will be prepared for analysis by combustion in a bomb containing oxygen under pressure (ASTM D808-63). The chlorine compounds thus liberated are absorbed in a sodium carbonate solution. Carbonate solutions and bomb rinsings are analyzed by ion chromatography. Water samples do not require preparation.

The absorbing solutions from Parr bomb combustions and the water samples will be directly injected into the IC sample loop. The Dionex Model 14 Ion

Chromatograph provides for the simultaneous determination of chloride, fluoride and bromide. Analysis is accomplished by the absorption of the sample aliquot on a series of ion-exchange resin columns. Subsequently the anions are eluted via dilute sodium carbonate/sodium bicarbonate solution and quantified by means of conductance. The selectivity of IC eliminates the difficulties encountered when utilizing gravimetric determinations in oils. Interferences due to metals content and other halogens precipitated by silver ions which present difficulties in gravimetric analysis of Cl are easily resolved by IC. The limit of detection normally achievable for chloride in solution is 0.2 ppm.

8.0 DATA REDUCTION, VALIDATION AND REPORTING

8.1 DATA REDUCTION

Analysis results will be reduced to concentration units specified in EPA's instructions or the analytical procedure, using the equations given in the analytical procedures. If units are not specified, data from the analysis of fuel oils will be reported in units of mg/kg. Appropriate blank corrections will be applied in all cases.

8.2 DATA VALIDATION

Data validation is the process of filtering data and accepting or rejecting it on the basis of sound criteria. GCA/Technology Division supervisory and QC personnel will use validation methods and criteria appropriate to the type of data and the purpose of the measurement. Records of all data will be maintained, even that judged to be an "outlying" or spurious value. Outliers will be identified using Dixon's test[6] for extreme observations or the one-tailed t-test for difference. The persons validating the data will have sufficient knowledge of the technical work to identify questionable values.

Analytical data generated in this program will be considered valid if the analytical systems are demonstrated to be in control before and after analysis of oil samples. As noted in this plan, control limits are provided for all instruments and they must be met before analysis of field samples.

9.0 INTERNAL QUALITY CONTROL CHECKS

Quality control checks are performed to monitor the collection and handling of samples and the generation of valid analytical results on these samples. These checks are performed by project participants throughout the program under the guidance of the QA Manager and the Project QC Coordinator.

GCA's Quality Control program for laboratory analysis makes use of a number of different types of QC samples to document the validity of the generated data. The following types of QC samples are used routinely by GCA to monitor measurement systems:

1. Blank Samples

   a. Method Blanks--Blanks which are processed through the sample preparation procedures to account for contamination introduced in the laboratory. One method blank is prepared with each batch of 20 or fewer samples processed.

      Calibration Blanks--Blanks used in instrument calibration; these blanks contain the reagents used in preparing instrument calibration standards except the parameters of interest.

2. Duplicate Samples

   Laboratory Duplicates--A second aliquot of a sample carried through all sample preparation and analysis procedures to estimate the precision of the analytical method. At least one sample in each analysis batch of 20 or fewer samples is analyzed in duplicate.

3. Spiked Samples--At least one sample in each analysis batch of 20 or fewer samples will be spiked with the parameters of interest at a level two or three times the method detection limit.

The duplicate and spiked samples may be submitted as known QC samples, termed laboratory control samples (LCS), or "blind" QC samples, those which are not recognizable to the analyst. LCS are routinely used to ensure that the analytical process is in control.

Reagents used in the laboratory are normally of analytical reagent grade or higher purity; each lot of acid or solvent used is checked for acceptability prior to lab use. All reagents are labeled with the date received and date opened. The quality of the laboratory deionized water is routinely checked.

10.0 QUALITY ASSURANCE PERFORMANCE AUDITS, SYSTEM AUDITS AND FREQUENCY

GCA/Technology Division's quality assurance program includes both performance and system audits as independent checks of the quality of data obtained from sampling, analysis, and data gathering activities. Every effort is made to have the audit assess the measurement process in normal operation. Either type of audit may show the need for corrective action.

10.1 PERFORMANCE AUDITS

The samkpling, analysis, and data handling segments of a project are checked in performance audits. A different operator/analyst performs these audit operations to ensure the independence of the quantitative results.

In this program, EPA Quality Control concentrates and NBS Standard Reference Materials will be used to assess the analytical work. The Laboratory QC Coordinator will direct the inclusion in the sample load of QC samples appropriate to the analyses performed so that they are not recognizable to the analyst. In addition, any appropriate interlaboratory study samples which are available during this program will be analyzed to further audit the analytical work.

10.2 SYSTEM AUDITS

A system audit will be conducted by the Division QA Manager at least once during the program to ensure that the elements outlined in the QA Plan are functioning.

11.0 PREVENTIVE MAINTENANCE

GCA/Technology Division follows an orderly program of positive actions to prevent the failure of equipment or instruments during use. This preventive maintenance and careful calibration help to ensure accurate measurements from field and laboratory instruments.

In the analytical laboratories preventive maintenance includes attention to glassware, water supply, reagents, analytical balances, as well as more complex instrumentation. Table 11-1 summarizes routine maintenance procedures and frequency for the analytical equipment to be used in this program. It is assumed that the instruments will need very frequent cleaning because of the viscosity and complexity of the oil samples. The analysts are alert to this need and will use the cleaning and maintenance procedures provided in the instrument manufacturers' manuals.

TABLE 11-1. MAINTENANCE PROCEDURES AND SCHEDULE FOR MAJOR INSTRUMENTATION

Instrument	Maintenance procedure/schedule	Spare parts
Dohrmann DX-20 Total Organic Halide Analyzer	1. Clean/lubricate push rods as needed.	1. Relay switches
	2. Clean valves as needed.	2. Cartridge holders
Dionex Model 14 Ion Chromatograph	1. Check all valves and column fittings for leaks daily.	1. Millipore filter unit for syringes.
	2. Check all air and liquid lines for crimping or discoloration weekly.	2. Anion precolumn.
	3. Oil instrument pumps monthly.	3. Plastic syringes.
Hewlett-Packard 5993/5985 GC/MS	1. Replace pump oils annually.	1. Syringes.
	2. Change septa daily.	2. Septa.
	3. Change gas line dryers quarterly.	
	4. Replace electron multiplier as needed.	

12.0 ASSESSMENT OF DATA PRECISION, ACCURACY AND COMPLETENESS

12.1 PRECISION ESTIMATES

Replicate analyses will be conducted for each pollutant. The standard deviation of these replicate measurements will be used to estimate the overall measurement precision. The following equation will be used to calculate standard deviation:

$$S = \sqrt{\frac{\sum_{i=1}^{N} X_i^2 - \frac{1}{N}\left(\sum_{i=1}^{N} X_i\right)^2}{N-1}}$$

where S = standard deviation

X_i = individual measurement results

N = number of measurements

Relative standard deviation may also be reported. If so, it will be calculated as follows:

$$RSD = 100 \frac{S}{\overline{X}}$$

where RSD = relative standard deviation, expressed percent

S = standard deviation

$\overline{X}$ = arithmetic mean of replicate measurements

12.2 ACCURACY ESTIMATES

During this program, measurements will be made on samples whose true values are known to QA/QC personnel but not to the person making the measurement. Accuracy will be expressed as percent recovery or as relative error. The formulas to calculate these values are:

$$\text{Percent Recovery} = 100 \left(\frac{\text{Measured Value}}{\text{True value}}\right)$$

$$\text{Relative Error} = 100 \left(\frac{\text{Measured Value} - \text{True Value}}{\text{True Value}}\right)$$

12.3 COMPLETENESS

Completeness will be reported as the percentage of all measurements made whose results are judged to be valid. The criteria given in this QA Plan will be used to determine what data are valid. Completeness will be estimated by:

$$\text{Completeness} = 100 \left(\frac{\text{Number of Measurements Judged Valid}}{\text{Total Number of Measurements}}\right)$$

13.0 CORRECTIVE ACTION

Perhaps the single most important part of any quality assurance program is a well-defined, effective policy for correcting quality problems. GCA/Technology Division maintains a closed-loop corrective action system under the direction of the QA Manager with full management support. While the entire quality assurance program operates to prevent problems, it also serves to identify and correct those that may exist. Usually these quality problems require either on-the-spot, immediate corrective action or long-term corrective action.

Specific QC procedures and checklists are designed to help field technicians and analysts detect the need for corrective action. Often the person's experience will be most valuable in alerting the operator to suspicious data or malfunctioning equipment.

If a corrective action can be taken at this point, as part of normal operating procedures, the collection of poor quality data can be avoided. Instrument and equipment malfunctions are most amenable to this type of action and GCA's QC procedures include troubleshooting guides and corrective action suggestions. The actions taken should be noted in field or laboratory notebooks but no other formal documentation is required, unless further corrective action is necessary. These on-the-spot corrective actions are an everyday part of the QA/QC system.

If the problem is not solved in this way, more formalized long-term corrective action may be necessary. The need for this action may be identified by standard QC procedures, control charts, performance or system audits. Any quality problem which cannot be solved by immediate corrective action falls into this long-term category. GCA uses a system to ensure that the condition is reported to a person responsible for correcting it who is part of the closed-loop action and follow-up plan.

The essential steps in the closed-loop corrective action system are:

- Identify and define the problem.
- Assign responsibility for investigating the problem.
- Investigate and determine the cause of the problem.

- Determine a corrective action to eliminate the problem.
- Assign and accept responsibility for implementing the corrective action.
- Establish effectiveness of the corrective action and implement it.
- Verify that the corrective action has eliminated the problem.

Documentation of the problem is important to the system. A Corrective Action Request Form is filled out by the person finding the quality problem. This form identifies the problem, possible causes and the person responsible for action on the problem. The responsible person may be an analyst, field team leader, project QA coordinator, or the QA Manager. If no person is identified as responsible for action, the QA Manager investigates the situation and determines who is responsible in each case.

For this program, acceptance limits have been provided in this plan for equipment calibration and internal QC procedures. If these limits are exceeded, corrective action will be initiated.

14.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

14.1 INTERNAL GCA REPORTING

Each department QC Coordinator reports to his department manager and the QA Manager routinely, and on any quality problem or need. The QA Manager will check with the QC Coordinators involved in this project on an ad-hoc basis in addition to the regular monthly review conferences she holds with them individually to discuss department concerns.

The Laboratory Analysis Department QC Coordinator maintains QC records and charts on instrument calibration, and performance on known and blind QC samples. She directs the preparation and inclusion of QC samples, blanks, and duplicates in the project sample load in a fashion unrecognizable to the analyst. She will review all routine laboratory QC results germane to this Technical Directive and initiate corrective actions as needed. These results, problems found, and actions taken will be included in her monthly written report to the Department and QA Managers.

All Corrective Action Forms are submitted to the QA Manager for initial approval of the corrective action planned and a copy is provided to the department manager. All system audit reports are provided to the project manager, department manager and the Technology Division General Manager.

14.2 REPORTS TO EPA

The Laboratory QC Coordinator will prepare a section for each monthly progress report summarizing QC activities on this project including:

- Estimates of precision, accuracy and completeness of reported data
- Results of performance audits, including pertinent interlaboratory studies
- System audit reports
- Quality problems found
- Corrective actions taken.

The QA Manager will aid in preparation of a section of the Final Report summarizing all QA/QC activities as stated above.

15.0 REFERENCES

1. Total Organic Halide Method 450.1 Interim, U.S. Environmental Protection Agency, EMSL/Cincinnati. November 1980.

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3. 1979 Annual Book of ASTM Standards, Part 23, Petroleum Products and Lubricants. American Society for Testing and Materials, Philadelphia, PA. 1979.

4. Envirotech/Dohrmann DX-20 Total Organic Halide Analyzer System, Santa Clara, CA. November 1979.

5. Federal Register, 3 December 1979. Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations, 40 CFR 136.

6. Dixon, W. J. Processing Data for Outliers, Biometrics, 9(1):74-89. 1953.

7. Sample Size Requirements for Surveying the Extent of Contaminated Heating Fuel in Metropolitan New York, letter with attachments from Dr. James Dunn (University of Alabama) to Joseph McSorley (U.S. Environmental Protection Agency), December 3, 1982.